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Final Guideline Document: Control of Sulfuric Acid Mist Emissions from Existing Sulfuric Acid Production Units

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GUIDELINE SERIES

FINAL GUIDELINE DOCUMENT: CONTROL OF SULFURIC ACID MIST EMISSIONS FROM EXISTING SULFURIC ACID PRODUCTION UNITS

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

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Emission Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

September 1977

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(Please read Instructions on the reverse before completing)

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16. ABSTRACT

The U. S. Environmental Protection Agency is required under 40 CFR Part 60 to publish a guideline document for development of State emission standards after promulgating any standard of performance for a designated pollutant. Standards of performance limiting emissions of such a designated pollutant--sulfuric acid mist--from new and modified sulfuric acid production units were promulgated on December 23, 1971, necessitating the development of this document. The document includes the following information: (1) Emission guidelines and times for compliance; (2) A brief description of the sulfuric acid industry, and the nature and source of acid mist emissions; (3) Information regarding the effects of acid mist on health and welfare; and (4) Assessments of the environmental, economic, and energy impacts of the emission guideline.

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1. INTRODUCTION AND SUMMARY

1.1 INTRODUCTION

Section 111(d) of the Clean Air Act, 42 U.S.C. 1857c-6(d), as amended, requires EPA to establish procedures under which States submit plans to control certain existing sources of certain pollutants. On November 17, 1975 (40 FR 53340) EPA implemented section 111(d) by promulgating Subpart B of 40 CFR Part 60 establishing procedures and requirements for adoption and submittal of State plans for control of "designated pollutants" from "designated facilities". Designated pollutants are pollutants which are not included on a list published under section 108(a) of the Act (National Ambient Air Quality Standards) or section 112(b)(1)(A) (Hazardous Air Pollutants), but for which standards of performance for new sources have been established under section 111(b). A designated facility is an existing facility which emits a designated pollutant and which would be subject to a standard of performance for that pollutant if the existing facility were new.

Subpart B of 40 CFR Part 60 provides that EPA will publish a guideline document for development of State emission standards after promulgation of any standard of performance for a designated pollutant. The document will specify emission guidelines and times for compliance and will include other pertinent information such as discussion of the pollutant's effects on public health and welfare and description of control techniques and their effectiveness and costs. The emission guidelines will reflect the degree of emission reduction attainable with the best adequately demonstrated systems of emission reduction, considering costs as applied to existing facilities.

After publication of a final guideline document for the pollutant in question, the States will have nine months to develop and submit plans for control of that pollutant from designated facilities. Within four months after the date for submission of plans, the Administrator will approve or disapprove each plan (or portions thereof). If a state plan (or portion thereof) is disapproved, the Administrator will promulgate a plan (or portion thereof) within six months after the date for plan submission. These and related provisions of subpart B are basically patterned after section 110 of the Act and 40 CFR Part 51 (concerning adoption and submittal of state implementation plans under section 110).

As discussed in the preamble to subpart B, a distinction is drawn between designated pollutants which may cause or contribute to endangerment of public health (referred to as "health-related pollutants") and those for which adverse effects on public health have not been demonstrated (referred to as "welfare-related pollutants"). For health-related pollutants, emission standards and compliance times in state plans must ordinarily be at least as stringent as the corresponding emission guidelines and compliance times in EPA's guideline documents (variances may be granted in cases of economic hardship and similar cases.

However, the Administrator may approve less stringent emission standards and compliance schedules on a case-by-case basis if the State provides sufficient justification. Justification for less stringent emission standards will be based on physical limitations or unreasonable cost of control resulting from the plant's age, location, or basic process design, and justification for less stringent compliance schedules may include unusual time delays caused by unavailability of labor, climatological factors, scarcity of strategic materials, and large work backlogs for equipment vendors or construction contractors.

For welfare-related pollutants, States may balance the emission guidelines, times for compliance, and other information provided in a guideline document against other factors of public concern in establishing emission standards and compliance schedules, and variances provided that appropriate consideration is given to the information presented in the guideline document and at public hearing(s) required by Subpart B and that all other requirements of Subpart B are met.

Standards of performance for new sulfuric acid production units were promulgated on December 23, 1971 (36 FR 24876) in Subpart H of 40 CFR Part 60. Section 60.83 of Subpart H sets forth a standard of performance for sulfuric acid mist, which is a designated pollutant. Therefore, the States are required to adopt sulfuric acid mist emission standards for existing contact sulfuric acid production units which would be subject to the standard of performance if they were new.

The Administrator has determined that sulfuric acid mist is a health-related pollutant. The rationale for this determination is included in Chapter 5 of this document.

This guideline document provides a brief description of the sulfuric acid manufacturing industry and the contact sulfuric acid process. Information is also provided regarding the nature and source of sulfuric acid mist and its health effects. The greatest emphasis, however, has been placed on the technical and economic evaluation of control techniques that are effective in reducing acid mist emissions, with particular emphasis on retrofitting existing plants.

1.2 SULFURIC ACID MIST

For purposes of standards of performance for new stationary sources (SPNSS) and the attendant requirements of section 111(d), the term sulfuric acid mist includes not only liquid mist but also sulfur trioxide (SO_3) and sulfuric acid vapor. All of these materials are measured by the reference method for acid mist - Method 8 - of Appendix A to 40 CFR 60. In addition, any of these materials which contribute to visible emissions are measured by Method 9 of Appendix A to 40 CFR 60.

The intent of the SPNSS is to limit emissions of liquid sulfuric acid mist, acid vapor, and SO_3. Control of these pollutants requires not only good initial plant design and a suitable mist eliminator, but also careful and proper operation of the absorber and of the overall sulfuric acid plant. Thus, the SPNSS requires control of more than liquid acid mist alone.

1.3 STANDARDS OF PERFORMANCE FOR NEW SULFURIC ACID PLANTS

In accordance with section 111 of the Clean Air Act, standards of performance were promulgated on December 23, 1971 (36 FR 24876 under §§60.82 and 60.83) for sulfur dioxide (SO_2) and acid mist emissions from new and modified contact-process sulfuric acid and oleum facilities that burn elemental sulfur, alkylation acid, hydrogen sulfide, organic sulfides, or acid sludge.

The standard does not apply to acid plants used as SO_2 control systems, to chamber process plants, acid concentrators, or to oleum storage and transfer facilities. The chamber process is being phased out and replaced by the contact process.

Standards of performance for new sulfuric acid plants state that no person shall cause to be discharged into the atmosphere from any affected facility any gases which contain sulfur dioxide (SO_2) in excess of 2 kg per metric ton of acid produced (4 lb per ton), the production being expressed as 100 percent H_2SO_4.

This standard requires that new sources either be designed for dual absorption or employ suitable scrubbing processes to meet the SO_2 limit.

Sulfur dioxide is a pollutant for which national ambient air quality standards have been promulgated. States are not required to submit plans to control SO_2 under section 111(d), although many states limit SO_2 emissions from sulfuric acid plants under section 110 of the Clean Air Act.

Standards of performance for acid mist from new sulfuric acid plants require that no person shall cause to be discharged into the atmosphere from any affected facility any gases which:

(1) Contain acid mist, expressed as H_2SO_4, in excess of 0.075

kg per metric ton of acid produced (0.15 lb per ton) the production being expressed as 100 percent H_2SO_4.

(2) Exhibit 10 percent opacity or greater.

For Method 8, the sampling time for each run shall be at least 60 minutes and the minimum sample volume shall be 1.15 dscm (40.6 dscf). For a typical sulfur burning plant feeding 8 percent SO_2 to the converter, uncontrolled acid mist emissions are about 4* pounds per ton (lb/ton) of 100 percent H_2SO_4 for an acid plant and 10 lb/ton for an oleum-producing plant. For this same plant, the acid mist standard of 0.15 pound per ton is equivalent to a concentration of 0.8 mg of sulfuric acid per standard cubic foot of effluent (see Figure 4.1). Equivalent volumetric concentrations in milligrams per standard cubic foot (mg/scf) will vary from plant to plant because they are dependent on the SO_2 concentration to the converter. The range 0.5 to 1.0 mg/scf will cover emissions from most contact acid plants covered by the new source performance standard.

1.4 CONTROL OF ACID MIST EMISSIONS FROM EXISTING PLANTS.

Good control of sulfuric acid mist emissions from existing contact sulfuric acid plants can be achieved through proper absorber operation and the installation of effective mist control devices. The latter include electrostatic precipitators and fiber mist eliminators. It is anticipated that most existing plants with ineffective control will elect to install fiber mist eliminators since they generally have lower installation and operating costs.

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*Although EPA's policy is to use the metric system, certain non-metric units are used in this document both for convenience and to reflect original data.

There are three types of fiber mist eliminators: vertical tube, vertical panel, and horizontal dual pad. Of these, vertical panel and horizontal dual pad mist eliminators are less effective and less expensive than vertical tube mist eliminators. They are suitable for at least 45 percent of the contact plants in the U. S. that burn only sulfur and produce sulfuric acid or weak oleum. The typical manufacturer guarantee for vertical panel and horizontal dual pad mist eliminators installed on these plants is 2 milligrams per cubic foot as measured by the Monsanto Method(a) which is equivalent to 0.3 to 1.5 lb/ton for most existing contact plants (See Figure 4.1).

EPA source tested two sulfur-burning acid-producing units using both EPA Method 8 and the Monsanto Method (see Section 6.3.2). One of these units was equipped with a vertical panel mist eliminator. Test results using EPA Method 8 ranged from 0.14 to 0.28 lb/ton, equivalent to concentrations of 0.55 to 1.11 mg/scf. Test results using the Monsanto Method ranged from 0.14 to 0.24 lb/ton, equivalent to concentrations of 0.56 to 0.94 mg/scf. The other unit was equipped with a horizontal dual pad mist eliminator. Test results using EPA Method 8 ranged from 0.05 to 0.10 lb/ton, equivalent to concentrations of 0.19 to 0.40 mg/scf. Test results using the Monsanto Method ranged from 0.07 to 0.13 lb/ton, equivalent to concentrations of 0.27 to 0.49 mg/scf. These test results indicate that even though the mist eliminators are only guaranteed for 2 mg/scf, they actually are doing much better applied to these two plants.

(a) Mention of a trademarked product or company name is not intended to constitute endorsement by the Environmental Protection Agency.

The most effective and expensive mist eliminator is the vertical tube. It is suitable for all contact plants. The typical manufacturer guarantees range from 90 to 99.8 percent control with 99.3 percent being most common. Generally speaking, the higher the efficiency, the higher the installed cost. Applying 99.3 percent control to a typical oleum-producing plant with an uncontrolled acid mist emission of about 10 lb/ton would result in an emission of 0.07 lb/ton. EPA source tested three units equipped with vertical tube mist eliminators using EPA Method 8 (see Section 6.3.1). Test results ranged from 0.01 to 0.15 lb/ton.

Data were obtained (Table 6.7) using EPA Method 8 by companies with plants making various strengths of oleum and burning various feedstocks. All three types of mist eliminators were represented and all acid mist emissions were below 0.5 lbs/ton. The high reading for horizontal dual pads was 0.38 lbs/ton and was for a case where spent acid was a feedstock. Another plant burned only H_2S, which practice is believed to result in almost 100 percent acid mist formation; the exit gas from the vertical tube mist eliminator ranged from 0.13-0.21 lbs/ton.

Data from industry (Table 6.8) confirms EPA belief that impaction devices - such as the horizontal dual pad mist eliminator - are relatively ineffective in removing submicron acid mist.

1.5 EMISSION GUIDELINE

The following emission guideline applies to existing sulfuric acid and oleum facilities that burn elemental sulfur, alkylation acid, hydrogen sulfide, organic sulfides, or acid sludge; it does not apply to acid plants used as SO_2 control systems, to chamber process plants, acid concentrators, or to oleum storage and transfer facilities. The emission guideline which reflects the application of the best system of emission reduction considering costs, is:

> Emissions from designated facilities can be limited to 0.25 g acid mist (as measured by EPA Method 8, of Appendix A to 40 CFR Part 60) per kg of acid produced (0.50 lb per ton) the production being expressed as 100 percent H_2SO_4.

For plants producing strong oleum and for plants not producing strong oleum, but burning chemically bound sulfur feedstock the vertical tube mist eliminator is usually needed for control to 0.25 g mist/kg (0.5 lb mist/ton) 100% H_2SO_4.

The November 1974 costs of adding vertical tube controls varies from \$60,000 to \$99,000 for the 50 ton/day of H_2SO_4 plant and from \$560,000 to \$900,000 for the 1500 ton/day plant. The range in cost for each model plant reflects the degree of retrofit difficulty for installation of the control device. The corresponding annualized costs of control are $0.92 to $1.69 per ton of H_2SO_4 for the 50 ton/day plant and $0.29 to $0.56 for the 1500 ton/day plant (Table 6.2).

Vertical panel and horizontal dual pad mist eliminators are suitable controls for plants producing sulfuric acid and/or oleum up to about 20 percent in strength. For these types of plants, a control level of 0.25 g/kg 100% H_2SO_4 is readily achieved. Some acid plant owners have claimed instances where these controls have sufficed for stronger oleums and bound sulfur feedstocks (Table 6.7).

The costs of adding vertical panel or horizontal dual pad mist eliminators to an existing plant varies from $19,000 to $52,000 for the 50 ton/day H_2SO_4 plant and $90,000 to $620,000 for the 1500 ton/day plant. The range in costs for each model plant, as stated earlier for the vertical tube, reflects the degree of retrofit difficulty. The corresponding annualized costs of control are $0.32 to $0.86 per ton of H_2SO_4 for the 50 ton/day plant and $0.03 to $0.37 for the 1500 ton/day plant (Table 6.2). The least cost alternative is the horizontal dual pad mist eliminator.

Section 7.4 estimates the number of plants that would be forced to double retrofit (retrofit to a stricter control level after previously retrofitting to a less stringent one) to reach a standard of 0.15 lb/ton. Of U. S. plants that burn sulfur and do not produce oleum, 55 - 80 percent would be forced to so retrofit. Thus, emission standards less than 0.5 lb/ton may have an excessive financial impact.

However, where double retrofitting is not a problem (i.e., in States with plants in compliance with existing standards more stringent than the guideline, or for presently uncontrolled plants), State standards as low as the standard of performance for new sources (0.15 lb/ton) may be justified.

1.6 COMPLIANCE TIMES

As can be seen from Table 1.1, the compliance times for installation of a mist eliminator on a sulfuric acid plant will not differ very much according to the type of device installed.

TABLE 1.1

COMPLIANCE TIMES FOR MIST ELIMINATOR INSTALLATION

MILESTONES	Elapsed Time, Weeks
State standard effective	0
Submit final control plan to agency	18
Award demister contract	26
Initiate demister installation	40 - 70
Complete demister installation	43 - 73
Final compliance achieved	44 - 74

The above milestones in the compliance times were derived from Table 6.1. The first two milestones above can probably be met in most cases; under favorable conditions, the times may be shorter. The interval between milestone 3 and 4 is that required for fabrication, including shipping. The fabrication time is almost completely out of the control of either the customer or the air pollution control official. For this reason, a range of elapsed time has to be given for fabrication. If possible, enforcement officials should try to consider each plant on a case-by-case basis and should require proof for the time requirements claimed for each milestone.

1.7 IMPACTS

Since the emission guideline is not an enforceable regulation applicable to any source, there is no direct impact from the emission guideline. Rather, the impacts result from State actions, and the degree to which States justify less stringent standards will determine the overall impact. In the discussion of impacts that follow, it will be assumed that all plants will be subject to a standard at least as stringent as the emission guideline.

Industry-wide adverse economic impacts are not expected for the emission guideline of 0.5 lb/ton. Only the sludge plant that operates extensively in competitive markets may find difficulty in absorbing the control costs or passing them in the form of higher prices to its merchant acid plants. The petroleum refiner who needs the services of this sludge processor either must pay the higher price of reclaimed acid, that reflects increased control costs, or invest the capital in his own new sludge plant. In consideration of the expense of the latter, he will probably choose paying higher prices to the affected sludge plant processor.

Depending on their product mix of sulfuric acid and oleum, oleum producers will pass on to a greater or lesser extent their control costs. Most oleum producers generally produce both acid and small amounts of oleum. Vendors refuse to guarantee the performance of pads and panels on oleum plants, and most States with standards require a limitation of 0.5 lb/ton or lower. For these reasons, occasional oleum producers would have installed vertical tubes and/or adjusted their market position in response to increased control costs.

The assessment of the environmental impact of the guideline is based on the incremental impact above that normally imposed on the environment by the affected sources or process controlled to meet other pollution regulations. The environmental impact is therefore a function of incremental effects, or a comparison of two degrees of control, and is not the total effect of the pollution control itself.

The most common State acid mist regulation is 0.5 lb acid mist/ton H_2SO_4, a level adopted by 10 of the 18 States with enforceable regulations.of which four have lower standards. (Table 6.9). Thus, the major impacts will occur in the 23 states with no standards with minor impacts occurring in the four States with less stringent standards. On a national basis, each emission increment of 0.1 lb/ton is equivalent to about 1600 tons/yr of acid mist, at current H_2SO_4 production level from about 215 plants in 41 states. However, the majority of plants have some type of mist eliminator and thus, the impact even in States with no regulation for acid mist is difficult to determine.

Other environmental impacts are absent, for all practical purposes. There is no effluent discharge at any acid mist control level. Acid mist controls do not generate solid waste. They do not change the quantity of SO_2 emitted.

2. SULFURIC ACID MANUFACTURING STATISTICS

2.1 DEFINITIONS.

Within this document, sulfuric acid plants are classified by product concentration and by type of feedstock. These classes are defined as follows:

1. Acid Plants - Plants that produce sulfuric acid, but no oleum.
2. Oleum Plants - Plants that produce oleum of any strength and that may also produce sulfuric acid simultaneously. Oleum is a solution of free, uncombined sulfur trioxide (SO_3) in sulfuric acid (H_2SO_4). Oleums are described in terms of their free SO_3 content. For example, a 20 percent oleum contains 20 percent free SO_3 and 80 percent H_2SO_4.
3. Sulfur Burning Plants - Plants that burn only elemental sulfur.
4. Bound Sulfur Feedstock Plants - Plants that burn chemically bound sulfur feedstocks, such as alkylation acid, hydrogen sulfide, or acid sludge, and that may also burn elemental sulfur.

2.2 EXISTING PLANTS.

2.2.1 Introduction

Sulfuric acid is one of the largest volume industrial chemicals produced in the United States. The United States is the world's leading producer of sulfuric acid. U.S. production in 1970 totalled 29.5 million short tons compared to a world total of 100.5 million short tons (1). U.S. production capacity in March 1971 was estimated at 38.6 million short tons and was accounted for by 251 plants (2). Of these, contact process plants totalled 214 and accounted for over 97 percent of U.S. production capacity (2) and 99 percent of U.S. production (3). The remaining 37 plants utilized the older lead chamber process. In 1973, U.S. production totalled 31.7 million short tons (3), and production capacity was estimated at 41.0 million short tons (4).

Sulfuric acid is produced in a variety of concentrations and in four grades: commercial; electrolyte or high purity; textile with low organic content; and chemically pure (C.P.) or reagent grade. Typical concentrations are: 35, 65, 78, 93 and 98 percent acid and 20, 30, 40, 50, 60, 65 and 100 (pure SO_3) percent oleum. The chief uses of sulfuric acid are in the production of phosphate fertilizer, the manufacture of chemicals, oil refining, pigment production, iron and steel processing, synthetic fiber production, and metallurgical applications.

Most sulfuric acid is consumed near its point of manufacture, by either the producer or nearby industries. Very little is shipped more than 300 miles. Of the 31.7 million short tons produced in the U.S. in 1973, 13.2 million tons were shipped at a value of 242 million dollars (3).

2.2.2 Location and Size

Table 2.1 is a listing of contact process sulfuric acid plants including location, capacity, age, type of feed, and oleum/acid production. It is based upon a census of sulfuric acid plants published in the Chemical Construction Company report (2), revised with information in Hydrocarbon Processing (5), CE Construction Alert in Chemical Engineering (6), supplements to the Stanford Research Institute Directory of Chemical Producers (7), and Control Techniques for Sulfur Oxide Air Pollutants (8).

Table 2.2 gives a size distribution of sulfuric acid establishments in the U.S. based on the Stanford Research Institute 1973 Directory of Chemical Producers (4).

The Chemical Construction Company report (2) and the Directory of Chemical Producers (4)(13) contain the only publicly-available plant-by-plant listings of sulfuric acid plants (or establishments). There is no trade association specific to the sulfuric acid industry, and plant-by-plant listings were not available from the Manufacturing Chemists Association or the U.S. Department of Commerce.

2.2.3 Type of Process

Table 2.3 is a summary of the number and capacity of U.S. single absorption contact sulfuric acid plants arranged by feed, conversion stages, and oleum/acid production. The table is based on

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TABLE 2.1

CONTACT PROCESS ACID PLANTS (a)

Company	City & State	Daily Capacity Short Tons	Year Built (b)	Principal Raw Materials (c)	Highest Concentration Product (d)
	Alabama				
Mobil Chem. Co.	Birmingham	70	1938	Sulfur	< 99% Acid
American Cyanamid Co.	Mobile	75	1947	"	"
Mobil Chem. Co.	Dothan	70	1966	"	"
DuPont	Mineral Springs	60	Pre 1954	"	Oleum
Reichhold Chem. Inc.	Tuscaloosa	150	1956	"	"
Stauffer Chem. Co.	LeMoyne	400	1956	"	"
	Arizona				
Bagdad Copper Corp.	Bagdad	175	1961	Sulfur	<99% Acid
Phelps Dodge Corp.	Morenci	600	1965	Cu Smelter Gas	Oleum
Phelps Dodge Corp.	Morenci	175	1968	" " "	"
Kennecott Copper Corp.	Ray	750	1968	" " "	< 99% Acid
American Smelting & Refining	Hayden	750	1971	Smelter Gas	-
Phelps Dodge Corp.	Ajo	-	1972	-	-
(e) **Inspiration Consolidated Copper Co.**	Inspiration	1330	-	Cu Smelter Gas	-
(e) **Kennecott Copper Corp.**	Hayden	-	1973	Cu Smelter Gas	-
Magma Copper Co.	San Manuel	1430	1974	Cu Smelter Gas	-
Heela Mining	Pinal County	270	-	-	-

Note: See p. 2-21 for footnotes.

TABLE 2.1 - PAGE 2

Company	City & State	Daily Capacity Short Tons	Year Built (b)	Principal Raw Materials (c)	Highest Concentration Product (d)
	Arkansas				
Monsanto Co.	ElDorado	375	Pre 1954	Sulfur	< 99% Acid
Gardinier Corp.	Helena	600	1967	"	"
Olin	N. Little Rock	250	1947	Sulfur & H_2S	Oleum
Cerro Corporation	Pine Bluff	400	-	Cu Smelter Gas	-
	California				
Allied Chemical Corp.	Nichols	350	Pre 1954	Sulfur	< 99% Acid
Occidental Petroleum Corp.	Lathrop	700	1957	"	"
Valley Nitrogen Prod. Inc.	Helm	200	1959	"	"
Valley Nitrogen Prod. Inc.	Helm	300	1963	"	"
Valley Nitrogen Prod. Inc.	Helm	600	1965	"	"
AFC Inc.	Edison	200	1967	"	"
Monsanto Co.	Avon	300	1953	Sludge & H_2S	Oleum
American Smelting & Refining	Selby	50	Pre 1954	Smelter Gas	< 99% Acid
(e) Standard Oil Co. of California	El Segundo	300	1972	Sludge & H_2S	"
Stauffer Chem. Co.	Dominquez	650	Pre 1954	" "	"
Allied Chemical Corp.	Richmond	200	1943	" "	"
Allied Chemical Corp.	Richmond	300	1955	" "	"
Union Oil Co. of California	Los Angeles	325	1960	" "	"
Stauffer Chem. Co.	Richmond	500	Pre 1954	Sulfur	Oleum
Stauffer Chem. Co.	Vernon	300	Pre 1954	"	"
Stauffer Chem. Co.	Martinez	850	1969	"	"
Valley Nitrogen Prod., Inc.	Helm	940	1975	"	< 99% Acid

TABLE 2.1 - PAGE 3

Company	City & State	Daily Capacity Short Tons	Year Built (b)	Principal Raw Materials (c)	Highest Concentration Product (d)
	Colorado				
Union Carbide Corp.	Uravan	175	1960-65	Sulfur	< 99% Acid
	Delaware				
Allied Chemical Corp.	N. Claymont	1,000	Pre 1954	Sludge + Pyrites	Oleum
	Florida				
Mobil Chem. Co.	Nichols	300	Pre 1954	Sulfur	< 99% Acid
W. R. Grace & Co.	Bartow	700	Pre 1954	"	"
Inter. Min. & Chem. Corp.	Bartow	600	Pre 1954	"	"
Swift & Co.	Agricola	900	1948	"	"
Mobil Chem. Co.	Nichols	600	1955-59	"	"
Gardinier, Inc.	Tampa	900	1955-59	"	"
Gardinier, Inc.	Tampa	900	1955-59	"	"
Gardinier, Inc.	Tampa	900	1955-59	"	"
Gardinier, Inc.	Tampa	900	1955-59	"	"
W. R. Grace & Co.	Bartow	700	1955-59	"	"
F. S. Royster Guano Co.	Mulberry	1,100	1960-65	"	"
Mobil Chem. Co.	Nichols	650	1960-65	"	"

TABLE 2.1 - PAGE 4

Company	City & State	Daily Capacity Short Tons	Year Built (b)	Principal Raw Materials (c)	Highest Concentration Product (d)
	Florida (cont.)				
CF Industries	Bartow	900	1960-65	Sulfur	<99% Acid
CF Industries	Bartow	600	1960-65	"	"
Inter. Min. & Chem. Corp.	Bartow	400	1960-65	"	"
CF Industries	Bartow	900	1962	"	"
Armour Agr. Chemical Co.	Ft. Meade	1,500	1963	"	"
Armour Agr. Chemical Co.	Bartow	800	1964	"	"
CF Industries	Bartow	900	1964	"	"
Continental Oil Co./Agrico Chem.	Pierce	2,000	1964	"	"
Borden Chem. Co./Smith Douglas	Plant City	1,400	1966	"	"
CF Industries	Plant City	1,700	1966	"	"
Farmland Ind. Inc.	Green Bay	1,570	1966	"	"
W. R. Grace & Co.	Bartow	1,100	1966	"	"
Occidental Petroleum Corp.	White Springs	2,000	1966	"	"
Farmland Industries	Bartow	2,200	1971	"	"
CF Industries	Plant City	2,850	1974	"	"
W.R. Grace & Co.	Bartow	2,000	1976	"	"
Inter. Min. & Chem. Corp.	New Wales	5,650	1975	"	"
(e) Occidental Petroleum Corp.	White Springs	3,600	1975	"	"
	Georgia				
Kaiser Agr. Chem. Company	Savannah	100	1952	Sulfur	<99% Acid
American Cyanamid Co.	Savannah	450	1953	"	"
American Cyanamid Co.	Savannah	250	1956	"	"
Minerals & Chem./Philipp Corp.	Attapulgas	100	1956	"	"
Cities Service Co. Inc.	Augusta	375	1967	"	"

TABLE 2.1 - PAGE 5

Company	City & State	Daily Capacity Short Tons	Year Built (b)	Principal Raw Materials (c)	Highest Concentration Product (d)
	Hawaii				
Standard Oil Co. of California	Honolulu	115	1960-65	Sludge	< 99% Acid
	Idaho				
J. R. Simplot Co.	Pocatello	650	1959	Sulfur	< 99% Acid
J. R. Simplot Co.	Pocatello	1,200	1966	"	"
Bunker Hill Co.	Kellogg	250	1954	Zn Smelter Gas	"
Bunker Hill Co.	Kellogg	350	1966	" " "	"
Bunker Hill Co.	Kellogg	300	1971	Pb	"
(e)Agricultural Products Corp.	Conda	850	1974	Sulfur	"
Agricultural Products Corp	Conda	1,000	196?	Sulfur	"
	Illinois				
Allied Chemical Corp.	Chicago	400	Pre 1954	Sulfur	<99% Acid
Swift & Co.	Calumet City	100	1947	"	"
Borden Chem. Co./Smith Douglas	Streator	125	1951	"	"
National Distillers Chem. Corp.	Tuscola	500	1953	"	"
American Zinc Co.	Sauget	400	1960-65	"	"
Beker Industries	Marseilles	700	1962	"	"
Wilson Co. Inc.	Elwood	600	Pre 1954	Sulfur + Sludge	Oleum
Charles Pfizer Co. Inc.	East St. Louis	18	Pre 1954	Ferrous Sulfate	<99% Acid

TABLE 2.1 - PAGE 6

Company	City & State	Daily Capacity Short Tons	Year Built (b)	Principal Raw Materials (c)	Highest Concentration Product (d)
	Illinois (cont.)				
American Zinc Co.	East St. Louis	450	1967	Zn Smelter Gas	<99% Acid
Allied Chemical Corp.	East St. Louis	500	1928	Sulfur	Oleum
Olin	Joliet	1,000	1942	"	"
American Cyanamid Co.	Joliet	150	1954	"	"
Monsanto Co.	Sauget	600	1967	"	"
(e) U.S. Army Corps of Engineers	Joliet	775	1973	Sludge	<99% Acid
Illinois Power Co.	Wood River	-	-	-	-
Anlin	Wood River	240	1973	Sludge + H_2S + Sulfur	<99% Acid
National Distillers Chem. Corp.	Tuscola	1,410	1975	-	-
	Indiana				
Stauffer Chem. Co.	Hammond	400	1929	Sludge + Sulfur	Oleum
DuPont	East Chicago	950	Pre 1954	Zn Smelter Gas + Sludge	"
Stauffer Chem. Co.	Hammond	500	1957	Sludge + Sulfur	"
Marion Mfg. Co.	Indianapolis	125	1947	Sludge + Sulfur	"
	Iowa				
Inter. Min. + Chem. Corp.	Mason City	70	Pre 1954	Sulfur	<99% Acid
Sinclair Petrochemicals Inc.	Ft. Madison	1,500	1968	"	"
National Distillers Chem. Corp.	Dubuque	150	1943	"	Oleum

TABLE 2.1 - PAGE 7

Company	City & State	Daily Capacity Short Tons	Year Built (b)	Principal Raw Materials (c)	Highest Concentration Product (d)
	Kansas				
Eagle Picher Co.	Galena	450	1954	Sulfur + Zn Smelter Gas	<99% Acid
National Distillers Chem. Corp.	DeSoto	250	1943	Sulfur	Oleum
	Kentucky				
DuPont	Wurtland	600	Pre 1954	Sulfur	Oleum
Pennsalt Chem. Corp.	Calvert City	125	1948	"	"
	Louisiana				
Olin	Bossier City	200	1929	Sulfur	<99% Acid
Allied Chemical Corp.	Baton Rouge	250	1954	"	"
American Cyanamid Co.	Fortier	100	1960-65	"	"
Baker Industries	Taft	1,500	1965	"	"
Allied Chemical Corp.	Geismar	1,500	1967	"	"
Freeport Chemical Co.	Uncle Sam	4,800	1968	"	"
Stauffer Chem. Co.	Baton Rouge	1,600	1969	Sulfur + Sludge	Oleum
Cities Service Co. Inc.	Lake Charles	450	1943	Sludge + H_2S	<99% Acid
DuPont	Burnside	1,500	1967	Sulfur + Sludge	Oleum
(e)Freeport Chemical Co.	Uncle Sam	1,600	1974	-	-
Agrico Chemical Co.	Donaldsonville	3,400	1974	-	-
Freeport Minerals Co.	Port Sulphur	250	1972	Waste Gas Sulfur Compounds	-

TABLE 2.1 - PAGE 8

Company	City & State	Daily Capacity Short Tons	Year Built (b)	Principal Raw Materials (c)	Highest Concentration Product (d)
	Maryland				
Bethlehem Steel Corp.	Sparrows Pt.	250	1953	Pyrites + H_2S	<99% Acid
Olin	Baltimore	300	1943	Sulfur	Oleum
Olin	Baltimore	200	1941	"	"
Olin	Baltimore	500	1940	"	"
W. R. Grace & Co.	Baltimore	400	1960-65	"	"
	Massachusetts				
Monsanto Co.	Everett	300	1969	Sulfur	Oleum
	Michigan				
W. R. Grace & Co.	Detroit	100	Pre 1954	Sulfur	<99% Acid
American Cyanamid Co.	Kalamazoo	70	1947	"	"
Continental Oil Co./Agrico Chem.	Bay City	100	1957	"	"
Allied Chemical Corp.	Detroit	600	1941	Sulfur + Sludge	Oleum
	Minnesota				
North Star Chem. Inc.	Pine Bend	205	1959	Sulfur & Sludge	<99% Acid

TABLE 2.1 - PAGE 9

	Company	City & State	Daily Capacity Short Tons	Year Built (b)	Principal Raw Materials (c)	Highest Concentration Product (d)
		Mississippi				
	Mississippi Chem. Corp.	Pascagoula	750	1958	Sulfur	<99% Acid
(e)	Mississippi Chem. Corp.	Pascagoula	1500	1972	Sulfur	-
(e)	Mississippi Chem. Corp.	Pascagoula	1500	1975	Sulfur	-
		Missouri				
	Missouri Lead Smelting Co.	Salem	200	1967	Zn or Pb Smelter Gas	<99% Acid
	St. Joseph Lead	Herculaneum	350	1969	Pb Smelter Gas	"
	W. R. Grace & Co.	Joplin	200	1960-65	Sulfur	Oleum
(e)	N.L. Industries, Inc.	St. Louis	900	1971	"	<99% Acid
	N.L. Industries, Inc.	St. Louis	450	1957	"	"
	Amax	Boss	290	1970?	Pb Smelter Gas	-
		Montana				
	Anaconda Co.	Anaconda	450	Pre 1954	Zn Smelter Gas	<99% Acid
(e)	Anaconda Co.	Anaconda	600	1973	Cu Smelter Gas	-
		Nevada				
	Anaconda	Yerington	400	1953	Sulfur + Ore	<99% Acid
	Kennecott Copper Corp.	McGill	1,237	-	-	-

TABLE 2.1 - PAGE 10

	Company	City & State	Daily Capacity Short Tons	Year Built (b)	Principal Raw Materials (c)	Highest Concentration Product (d)
		New Jersey				
	La Place Chem. Co.	Edison	200	1967	Sulfur	<99% Acid
	N L Industries, Inc.	Sayreville	300	1947	"	Oleum
	N L Industries, Inc.	Sayreville	300	1948	"	"
	N L Industries, Inc.	Sayreville	450	1950	"	"
	N L Industries, Inc.	Sayreville	450	1955	"	"
	Olin	Paulsboro	850	1959	Sulfur + Sludge	"
	Allied Chemical Corp.	Elizabeth	600	1957	" "	<99% Acid
	Allied Chemical Corp.	Elizabeth	600	1957	" "	"
	DuPont	Gibbstown	300	Pre 1954	Sulfur	Oleum
	DuPont	Linden	850	Pre 1954	"	"
	DuPont	Deepwater	350	Pre 1954	"	"
	American Cyanamid Co.	Warners	550	1928	"	"
	American Cyanamid Co.	Bound Brook	200	1940	"	"
	Essex Chem. Corp./Chems. Div.	Newark	500	1956	"	"
(e)	American Cyanamid	Linden (Warners)	700	1970	"	"
(e)	Cities Service	Monmouth Junction	100	1972	Iron-oxide roasting + sulfur	-
(e)	N L Industries, Inc.	Sayreville	-	1973	-	-
		New Mexico				
	Kerr McGee Chem. Corp.	Grants	400	1958	Sulfur	<99% Acid
	Climax Chemical Co.	Hobbs	150	1962	Sulfur + H_2S	"
	Kennecott Copper Corp.	Hurley	1,400	1974	Cu Smelter Gas	-
	Phelps Dodge	Hidalgo	-	-	-	-

TABLE 2.1 - PAGE 11

Company	City & State	Daily Capacity Short Tons	Year (b) Built	Principal Raw Materials (c)	Highest Concentration Product (d)
	New York				
Allied Chemical Corp.	Buffalo	550	Pre 1954	Sulfur	Oleum
Eastman Kodak Co.	Rochester	20	1930	"	"
	N. Carolina				
Mobil Chem. Co.	Wilmington	70	1944	Sulfur	< 99% Acid
Swift Co.	Wilmington	150	1955	"	"
Acme Chemical	Acme	170	1964	"	"
Texas Gulf Company	Lee Creek	3,050	1966	"	"
Armour Agr. Chemical Co.	Wilmington	200	1968	"	"
(e) Texas Gulf Company	Lee Creek	1525	1973	"	-
	Ohio				
Allied Chemical Corp.	Cleveland	350	Pre 1954	Sulfur	< 99% Acid
Diamond Fertilizer Co.	Sandusky	35	Pre 1954	"	"
DuPont	Cleveland	600	Pre 1954	"	"
Inter. Min. & Chem. Corp.	Lockland	100	Pre 1954	"	"
Mobil Chem. Co.	Cincinnati	40	1938	"	"
Minn. Mining & Mfg. Co.	Copley	175	1942	"	"
American Cyanamid Co.	Hamilton	250	1955	"	"

TABLE 2.1 - PAGE 12

Company	City & State	Daily Capacity Short Tons	Year Built (b)	Principal Raw Materials (c)	Highest Concentration Product (d)
	Ohio (cont.)				
Continental Oil Co./Agrico Chem.	Cairo	125	1960	Sulfur	<99% Acid
American Zinc Co.	Columbus	200	1967	Zn Smelter Gas	"
DuPont	North Bend	300	1955-59	Sulfur	Oleum
Coulton	Toledo	-	-	Sludge	-
	Oklahoma				
Ozark Mahoning Co.	Tulsa	360	1941	Hydrogen Sulfide	<99% Acid
National Zinc	Bartlesville	200	Pre 1954	Zn Smelter Gas + Sulfur	"
	Pennsylvania				
New Jersey Zinc Co.	Palmerton	500	Pre 1954	Zn Smelter Gas	Oleum
Witco Chem. Co. Inc.	Petrolia	100	1933	Sludge + Sulfur	"
Atlantic Richfield Co.	Philadelphia	400	1955-59	Sludge + H_2S	"
DuPont	Cornwells Hts.	200	Pre 1954	-	< 99% Acid
Allied Chemical Corp.	Newell	700	Pre 1954	Sulfur + Pyrite + Sludge	"

TABLE 2.1 - PAGE 13

Company	City & State	Daily Capacity Short Tons	Year Built (b)	Principal Raw Materials (c)	Highest Concentration Product (d)
	Pennsylvania (cont.)				
U. S. Steel Corp.	Neville Island	125	Pre 1954	Sulfur + H_2S	<99% Acid
Charles Pfizer Co. Inc.	Easton	35	1967	Ferrous Sulfate	"
St. Joseph Lead	Josephtown	300	1968	Zn Smelter Gas	"
Rohm and Haas Co.	Philadelphia	250	1929-54	Sulfur	"
St. Joe Minerals Corp.	Monaco	250	1972	-	-
	Rhode Island				
Essex Chemical	E. Providence	50	1929-49	Sulfur	<99% Acid
	S. Carolina				
W. R. Grace & Co.	Charleston	100	1955-59	Sulfur	<99% Acid
	Tennessee				
Cities Service Co. Inc.	Copperhill	650	1942	Iron Sulfide	Oleum
Cities Service Co. Inc.	Copperhill	950	1964	Iron Sulfide	Oleum
Cities Service Co. Inc.	Copperhill	1800	1972	Iron Sulfide	<99% Acid
Cities Service Co. Inc.	Copperhill	450	1954	Iron Sulfide	<99% Acid

TABLE 2.1 - PAGE 14

Company	City & State	Daily Capacity Short Tons	Year Built (b)	Principal Raw Materials (c)	Highest Concentration Product (d)
	Tennessee (cont.)				
U.S. Army Corps of Engineers	Tyner	400	Pre 1954	Sulfur	Oleum
U.S. Army Corps of Engineers	Chattanooga	580	1973	-	<99 % Acid
	Texas				
Olin	Pasadena	600	1947	Sulfur	<99% Acid
Borden Chem. Co./Smith Douglas	Texas City	450	1953	"	"
Phosphate Chem. Inc.	Pasadena	1,200	1960-65	"	"
Potash Co. of America	Machovec	45	1960-65	"	"
Occidental Petroleum Corp.	Plainview	300	1963	"	"
American Plant Food Corp.	Galena Park	400	1965	"	"
American Smelting & Refining Co.	Corpus Christi	200	Pre 1954	Zn Smelter Gas	Oleum
DuPont	La Porte	250	1955-59	Sludge + Sulfur	"
Du Pont	La Porte	750	1961	" "	"
Gulf Oil Corp.	Port Arthur	300	Pre 1954	Sludge + H_2S	<99% Acid
Stauffer Chem. Co.	Baytown	800	1955	Sludge	"
Olin	Beaumont	500	1957	Sludge + H_2S	<99% Acid
Shamrock Oil & Gas Corp.	Dumas	100	1958	" "	"
Texaco Inc.	Port Arthur	250	1965	" "	"
American Oil	Texas City	500	1969	Sludge	"

TABLE 2.1 - PAGE 15

Company	City & State	Daily Capacity Short Tons	Year Built (b)	Principal Raw Materials (c)	Highest Concentration Product (d)
	Texas (cont.)				
Olin	Port Arthur	200	Pre 1954	Sludge	Oleum
Stauffer Chem. Co.	Houston	1,750	Pre 1954	"	"
Stauffer Chem. Co.	Ft. Worth	350	Pre 1954	"	"
Stauffer Chem. Co.	Houston	2,000	1967	"	"
Olin	Houston	1,550	1972	-	-
(e) American Smelting & Refining Co.	El Paso	-	1972	Cu Smelter Gas	-
Chemical Producers Co.	El Paso	-	-	-	-
	Utah				
Kennecott Copper Corp.	Magna	750	Pre 1954	Cu Smelter Gas	<99% Acid
Kennecott Copper Corp.	Magna	400	1955-59	" " "	"
Kennecott Copper Corp.	Magna	500	1967	" " "	"
Kennecott Copper Corp.	Magna	-	1971	-	-
Kennecott Copper Corp.	Salt Lake City	500	1970	Smelter Gas	-
	Virginia				
American Cyanamid Co.	Piney River	85	1930	Sulfur	<99% Acid
Borden Chem. Co./Smith Douglas	Norfolk	200	1937	"	"

TABLE 2.1 - PAGE 16

Company	City & State	Daily Capacity Short Tons	Year Built (b)	Principal Raw Materials (c)	Highest Concentration Product (d)
	Virginia (cont.)				
Allied Chemical Corp.	Front Royal	400	1945	Sulfur	<99% Acid
Swift & Co.	Buell	135	1947	"	"
Weaver Fertlizer Co. Inc.	Norfolk	100	1955-59	"	"
Allied Chemical Corp.	Hopewell	400	1966	"	"
DuPont	Richmond	250	Pre 1954	"	Oleum
Hercules Powder	Radford	70	Pre 1954	"	"
(e) U.S. Army Corps of Engineers	Radford	500	1972	Sulfur + Sludge	<99% Acid
	Washington				
Georgia-Pacific Corp.	Bellingham	30	1965	Sulfur	<99% Acid
American Smelting & Refining Co.	Tacoma	200	Pre 1954	Smelter Gas	"
Allied Chemical Corp.	Anacortes	125	1958	Sludge + H_2S + Sulfur	"
	W. Virginia				
Allied Chemical Corp.	Nitro	400	1948	Sulfur	<99% Acid

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Company	City & State	Daily Capacity Short Tons	Year Built (b)	Principal Raw Materials (c)	Highest Concentration Product (d)
	Wisconsin				
DuPont	Barksdale	100	Pre 1954	Sulfur	Oleum
Olin	Baraboo	200	Pre 1954	"	"
U.S. Army Corps of Engineers	Baraboo	360	-	-	-
	Wyoming				
Western Nuclear Inc.	Riverton	200	1958	Sulfur	<99% Acid
Western Nuclear Inc.	Jeffrey City	125	1962	"	"

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FOOTNOTES:

(a) A "unit" is a single H_2SO_4 train. A "plant" is one or more units built at the same time and place. An "establishment" is one or more plants built at the same place but at different times. For plants built prior to 1954, the table does not usually differentiate between a plant and an establishment.

(b) For pre-1954, the exact year built is not available. Where time range is given, year built is within the range but the exact date is not available; except that a range given before 1954 may indicate an establishment of two or more plants built within the range.

(c) Plants listed as "sulfur" burn only sulfur; while plants not listed as "sulfur" may burn some sulfur.

(d) Plants listed as "oleum" also produce 98 or 93 percent acid.

(e) Indicates dual absorption plant.

TABLE 2.2

SIZE DISTRIBUTION OF SULFURIC ACID ESTABLISHMENTS IN THE U.S. (a)

Plant Capacity (100% H_2SO_4 equivalent)		
Tons/day	10^3 tons/yr	Number of Establishments
0 - 100	0 - 35	19
101 - 250	36 - 87	32
251 - 500	88 - 175	45
501 - 750	176 - 262	20
751 - 1000	263 - 350	18
1001 - 1500	351 - 525	15
1501 - 3000	526 - 1050	10
>3000	>1050	7
Not available		7
	Total	173

(a) The term "establishment" is defined in Table 2.1, p. 2-21, footnote (a).

TABLE 2.3

SUMMARY OF U. S. SINGLE ABSORPTION PLANTS (a)

Feed	Conversion Stages	Number			Capacity (10^6 tons/yr of 100% H_2SO_4 equiv.) Acid and Oleum
		Acid	Oleum	Total	
Sulfur	3	60	35	95	11.5
Sulfur	4	36	4	40	11.0
Sub-total		96	39	135	22.5
Bound Sulfur	3	36	24	60	7.5
Bound Sulfur	4	14	6	20	4.0
Sub-total		50	30	80	11.5
Totals		146	69	215	34.0

(a) The term "plant" is defined in Table 2.1, p. 2-21, footnote (a).

information in the Chemical Construction Company report (2), and gives the industry breakdown as of 1970. Most 3-stage plants were built prior to 1960, 4 stages being typical of plants built since 1960. Table 2.3 shows that while only 28 percent of the plants are 4-stage, they account for 44 percent of the total U.S. capacity. Table 2.3 also shows that 45 percent of the plants burn only sulfur and do not produce oleum; and that 32 percent of all the plants (sulfur and bound sulfur) do produce oleum.

Table 2.4 gives 1970 and 1973 acid and oleum production in the U.S. by the contact process (3). It shows that oleum production accounts for only 9-10 percent of the total contact process production.

Many of the sulfuric acid plants constructed since 1970 are dual absorption plants. As of October 1974, at least 14 dual absorption plants had been built in the U.S., with at least one more scheduled for completion by 1975. These are indicated in Table 2.1. The dual absorption process is operating successfully in over 90 plants throughout the world (9).

2.3 FUTURE TRENDS.

Table 2.5 shows the changes in acid production and in number of producing establishments for certain years since 1939 (3,10).

TABLE 2.4

CONTACT PROCESS ACID AND OLEUM PRODUCTION

(10^3 tons/year)

	1970	1973
Acid	26,243	28,743
Oleum		
Under 40%	2,021	2,137
40%	699	472
Over 40%	241	253
Total	2,961	2,862
Total-Contact Process	29,204	31,605

TABLE 2.5

GROWTH OF SULFURIC ACID INDUSTRY IN THE UNITED STATES

	Production (10^3 ton/yr of 100% H_2SO_4 equivalent)		Number of Producing Establishments (a)			
Year	New Acid (b)	Total Acid (b)	Contact Only	Chamber Only	Both	Total
1939	4,795	4,795	58	83	12	153
1945	8,687	9,522				
1949	10,727	11,432	94	83	10	187
1951	12,389	13,372				
1956	15,737	16,494	131	74	6	211
1960	17,085	17,883				
1961	17,058	17,848	144	65	5	214
1962	18,782	19,701				
1963	20,038	20,936	152	60	3	215
1964	21,959	22,924				
1965	23,751	24,790	156	51	3	210
1966	27,414	28,385				
1967	27,736	28,815	177	40	3	220
1968	27,404	28,544				
1969	28,233	29,537	169	30	1	200
1970	28,260	29,525				
1971	27,757	29,035	167	16	-	184
1972	29,980	31,184				
1973	30,557	31,723	161	8	-	169

(a) **The term "establishment" is defined in Table 2.1, p. 2-21, footnote (a).**

(b) "New acid" is defined as virgin acid or oleum produced from the oxidation of sulfur or sulfur-bearing material including the decomposition of sludge. "Total acid" includes new acid and also spent acid fortified (strengthened) by the addition of sulfur trioxide.

It shows a gradual retirement of plants using the old lead chamber process; a steady increase in production from 1939 to 1966, with only a slight increase from 1966 to 1973; and a peak in number of establishments from 1956 to 1967 and a gradual decline since then. Average annual production of new acid per establishment has increased from 31,400 tons in 1939 to 93,000 tons in 1963 and to 190,000 tons in 1973. This trend toward larger plant sizes is expected to continue. The approximate upper limit on unit sizes is now about 1500 tons per day (11).

Another significant change is the reduction in the ratio of production for merchant sales or shipments to production for captive use. In 1939 this ratio stood at 2:1 (merchant sales: captive), while in 1966 it stood at 1:1 and at 0.7:1 in 1973 (3,10).

Environmental pressures to recover industrial process wastes will probably bring about a higher percentage of spent acid and metallurgical plants in the future as contrasted to elemental sulfur plants.

EPA new source performance standards (Section 1.3) require SO_2 emission levels for new and substantially modified plants that cannot be met with single absorption unless a control device (such as a scrubber) is applied to the absorber tail gas. The standard thus requires either such tail gas treatment or the addition of a second absorber (dual absorption process). Dual absorption and three tail gas treatment systems are described in Section 3.1.3.

The importance of various regions of the country as acid-producing areas has also changed. Table 2.6 illustrates this change by presenting regional production figures for the years 1956, 1963, and 1970 (3, 10). The largest regional increase has occurred in the South, principally for the production of phosphate fertilizer. In 1963, approximately 40 percent of sulfuric acid produced in the U.S. was for phosphate fertilizer (10), while in 1971 about 50 percent went for fertilizer (12).

TABLE 2.6

PRODUCTION OF SULFURIC ACID IN THE U. S. BY REGIONS

Region	Production of New Acid (a) (10^3 tons/yr of 100% H_2SO_4 Equivalent)			Percentage of National Production		
	1956	1963	1970	1956	1963	1970
Northeast	2594.3	2810.2	2505.1	16.5	14.0	8.9
North Central	3516.7	4052.2	3661.1	22.3	20.2	13.0
South	7996.0	10832.9	18565.4	50.8	54.1	65.7
West	1630.3	2342.2	3528.3	10.4	11.7	12.5
	15737.3	20037.6	28259.9	100.0	100.0	100.0

(a) The term "new acid" is defined in Table 2.5, footnote (b).

2.4 REFERENCES FOR SECTION 2.

1. Chemical Economics Handbook Manual of Current Indicators. Menlo Park, California, Stanford Research Institute, August 1974.

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3. PROCESS DESCRIPTION

3.1 CONTACT SULFURIC ACID PRODUCTION. (1,2,3,4)

All contact processes incorporate three basic operations: burning of sulfur or sulfur-bearing feedstocks to form SO_2; catalytic oxidation of SO_2 to SO_3; and absorption of SO_3 in a strong acid stream. The several variations in the process are due principally to differences in feedstocks. The least complicated systems are those that burn elemental sulfur. Where appreciable organics and moisture exist, as in spent acid and acid sludge, additional operations are required to remove moisture and particulates prior to catalysis and absorption. The composition of feedstocks can affect the sulfur conversion ratio, the volume of exhaust gases and the character and rate of pollutants released.

3.1.1 Sulfuric Acid Plants Burning Elemental Sulfur

Figure 3.1 is a schematic diagram of a single absorption contact sulfuric plant burning elemental sulfur. Sulfur is burned to form a gas mixture which is approximately eight percent sulfur dioxide, 13 percent oxygen, and 79 percent nitrogen (by volume). Combustion air is predried by passing it through a packed tower circulating 98 or 93 percent sulfuric acid. This minimizes acid mist formation and resultant corrosion throughout the system.

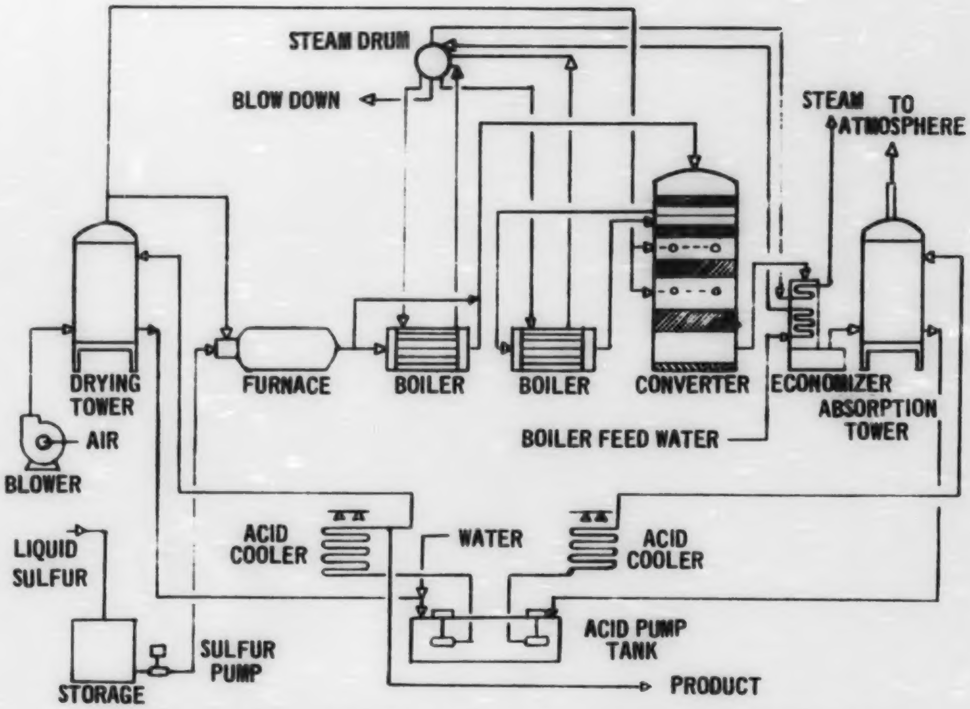

Figure 3.1. Contact-process sulfuric acid plant burning elemental sulfur.

The oxidation of sulfur dioxide (SO_2) to sulfur trioxide (SO_3) by oxygen is promoted by a vanadium pentoxide catalyst. The temperature of the reacting gas mixture increases as the reaction proceeds. Maximum conversion to SO_3 requires temperature limitation and several conversion stages with intermediate gas cooling. Most plants built prior to 1960 had only three conversion stages and overall conversion efficiencies were approximately 95 to 96 percent. Figure 3.1 shows four conversion stages which is typical of plants built after 1960. Efficiencies for these plants normally range between 96 and 98 percent. The gas exiting the converter is cooled in an economizer to 450° to 500°F, and SO_3 is absorbed in 98 percent sulfuric acid circulating in a packed tower. Water is in turn added to the acid to maintain the desired concentration. The absorber acid concentration and temperature must be carefully controlled to prevent excessive release of SO_3 and H_2SO_4 vapors.

A sulfuric acid plant can be designed to produce oleum in strengths up to 40 percent by the use of an oleum absorption tower between the converter and the final 98 percent acid absorber. The SO_3-laden gases from the converter are cooled and then passed through the oleum tower which is fed with acid from the 98 percent absorption system. The exit gas stream from the oleum tower is then passed through the final absorber for recovery of residual SO_3.

Oleum strengths greater than 40 percent are usually made by boiling off SO_3 from one oleum and absorbing it in another. The concentration of the SO_3 thus boiled off is higher than the concentration of the SO_3 in the process converter exit gas stream.

3.1.2 Sulfuric Acid Plants Burning Bound Sulfur Feedstocks

Where spent acid, sludge, and similar feedstocks are employed as a source of SO_2, the plants are more complex and expensive than sulfur-burning plants because the sulfur dioxide-containing gas stream is contaminated. Feed gases must be cleaned if high-quality acid is to be produced. This requires additional gas cleaning and cooling equipment to remove dust, acid mist, and gaseous impurities, along with excessive amounts of water vapor. (See Section 4.2 for discussion of acid mist formation). Purification equipment consists of cyclones, electrostatic dust and mist precipitators, plus scrubbers and gas-cooling towers in various combinations. Figure 3.2 shows one possible configuration of a spent acid plant. The balance of the process following the drying tower is essentially the same as an elemental sulfur-burning plant. Spent acid plants have followed the same design trend as sulfur-burning plants. Most three-stage plants were built prior to 1960 and four-stage plants were usually built after 1960. Comments on oleum production in Section 3.1.1 also apply to spent acid plants.

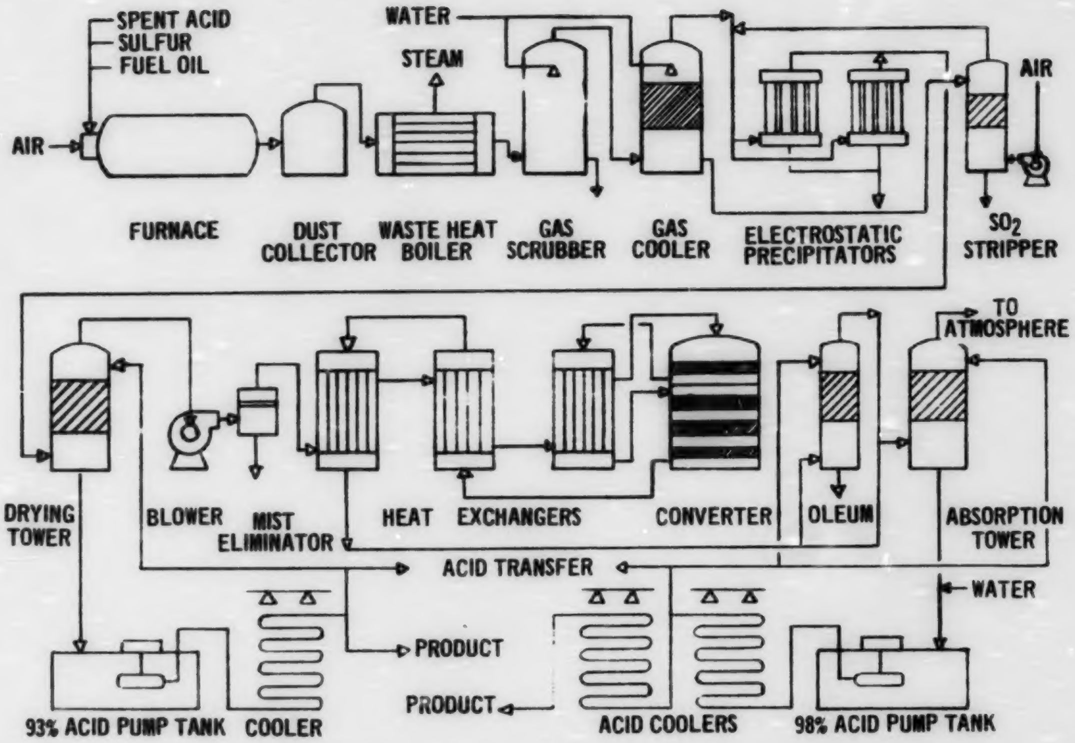

Figure 3.2. Contact-process sulfuric acid plant burning spent acid.

A few plants burning only hydrogen sulfide or hydrogen sulfide plus elemental sulfur use a simplified version of the above process. Wet gases from the combustion chamber and waste heat boiler are charged directly to the converter with no intermediate treatment. Gases from the converter flow to the absorber, through which 70 to 93 percent sulfuric acid is circulating. In a plant burning only hydrogen sulfide, all of the sulfur trioxide from the converter is in the form of acid mist, much of which is not absorbed in the absorption tower. High efficiency mist collectors both recover product acid and prevent excessive air pollution.

3.1.3 Dual Absorption Plants

In the dual absorption process, Figure 3.3, a greater fraction of the sulfur in the feedstock is converted to sulfuric acid than in the single absorption process. The SO_3 formed in the primary conversion stages is removed in a primary absorption tower and the remainder of the gas is returned to the final conversion stage(s). Removal of a product of a reversible reaction such as:

$$SO_2 + 1/2\ O_2 \rightleftarrows SO_3 \qquad (3.1)$$

drives the oxidation further toward completion, approaching the reaction equilibrium expressed by:

$$K = \frac{(SO_3)}{(SO_2)(O_2)^{1/2}} \qquad (3.2)$$

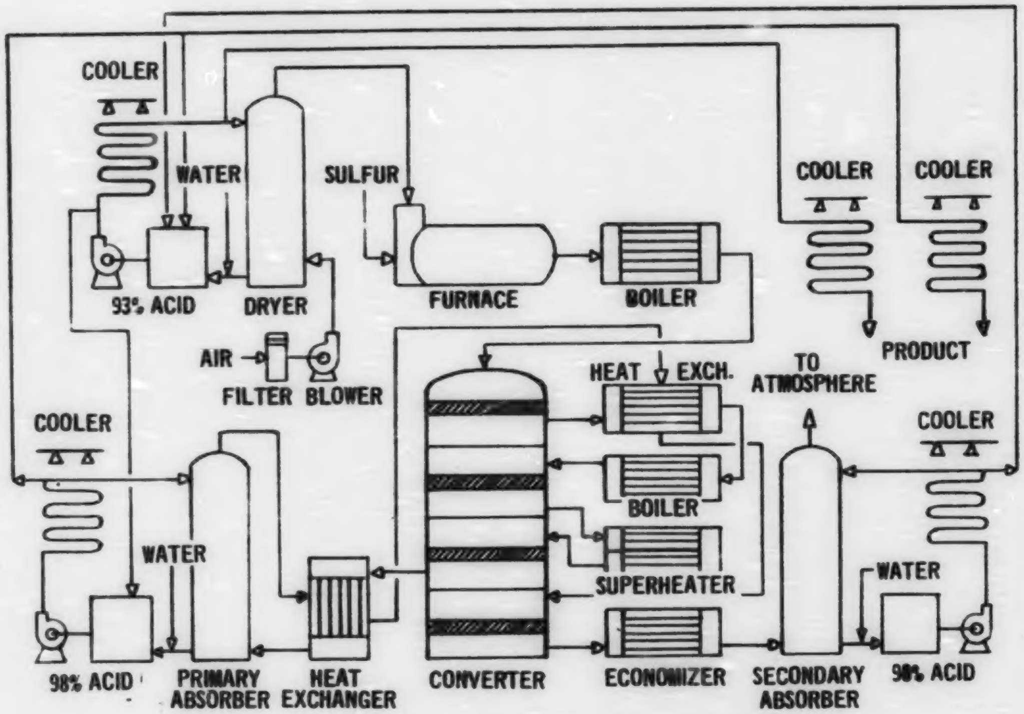

Figure 3.3. Dual absorption sulfuric acid plant.

where K is the reaction equilibrium constant peculiar to the temperature of the reaction and to the units of the parenthetical entities, which are usually taken as the molar concentrations of the gases involved.

The resulting SO_3 is absorbed in a secondary absorption tower obtaining at least 99.7 percent overall conversion of the sulfur to sulfuric acid.

Figure 3.3 depicts primary absorption after the third conversion stage with one final conversion stage. Dual absorption plants are also designed with primary absorption after the second conversion stage and two final conversion stages.

The dual absorption process permits higher inlet SO_2 concentrations than normally used in single absorption plants since the final conversion stage(s) effectively handles the residual SO_2 from the first conversion stages. Higher inlet SO_2 concentrations permit a reduction in equipment size which partially offsets the cost of the additional equipment required for a dual absorption plant. The dual absorption equipment occupies little more space than a conventional plant even though an additional absorber is required.

As shown in Table 2.1, the dual absorption process has been applied to sulfuric acid plants burning sulfur, spent acid and hydrogen sulfide; to metallurgical plants; and to plants producing acid and oleum. However, most applications have been for sulfur-burning and metallurgical plants producing acid only.

The 99.7 percent overall conversion efficiency of the dual absorption process corresponds to a stack emission of 4.0 pounds of SO_2 per ton of acid produced. This same low SO_2 emission level can be achieved in a single absorption plant by the use of a tail gas recovery system. In the United States, three such systems which have been commercially demonstrated to achieve this level or below are sodium sulfite scrubbing, ammonia solution scrubbing, and molecular sieve separation.

The sodium sulfite scrubbing system scrubs SO_2 from the tail gas yielding various percentages of sodium sulfite, bisulfite and sulfate in the spent scrubbing liquor (2). The bisulfite is then thermally decomposed to yield sodium sulfite crystals, SO_2, and water vapor. Most of the water vapor is condensed and the wet SO_2 is sent back to the acid plant. The crystals are separated from the mother liquor and are either dissolved in recovered condensate and recycled to the absorber or are consumed in the manufacture of other products. The mother liquor or spent scrubbing liquor must be purged to prevent sulfate buildup, and this purge stream is usually treated to reduce water pollution or may be dried for sale.

The ammonia solution scrubbing system scrubs SO_2 from the tail gas yielding various percentages of ammonium sulfite, bisulfite and sulfate (5). The spent scrubbing liquor can be converted to ammonium sulfate, if a market exists, or can be thermally decomposed to produce SO_2, nitrogen, and water vapor, the SO_2 being sent back to the acid plant. In the TVA "ABS" process, the ammonium sulfate is melted and decomposed to form ammonium bisulfate and ammonia gas which are both recycled.

The molecular sieve separation system removes SO_2 from the tail gas on an adsorbent bed (6). Just before the bed becomes completely saturated with SO_2, the feed gas is switched to an alternate bed and the saturated bed is regenerated with a purge of hot, dry air. The effluent purge stream, rich in SO_2, is fed back to the acid plant. The entire adsorption/regeneration cycle operates continuously on an automatically timed basis.

Relative acid mist production in dual vs. single absorption plants and the location of mist eliminators in the dual absorption process and in tail gas recovery systems is discussed in Section 4.3.

3.2 REFERENCES FOR SECTION 3.

1. Establishment of National Emission Standards for Stationary Sources. Vol. IV. Sulfuric Acid Plants. Research Triangle Institute and PEDCO - Environmental Specialists, Inc. Final Report. Contract CPA 70 - 164, Task Order No. 3, National Air Pollution Control Administration. Research Triangle Park, North Carolina. September 30, 1970. 43 p.

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4. ACID MIST EMISSIONS (1,2,3)

4.1 POINTS OF EMISSION.

The principal point of acid mist emission in a sulfuric acid plant is the exit gas from the final absorber, more commonly referred to as "stack gas" or "tail gas".

4.2 FORMATION AND CHARACTERISTICS.

Hexavalent sulfur is present in the stack gas as sulfuric acid vapor, gaseous sulfur trioxide (SO_3), and particulate acid mist.

4.2.1 Sulfuric Acid Vapor

The stack gas leaving the final absorber always contains sulfuric acid vapor. This vapor is in equilibrium with the acid in the absorber at its operating acid concentration and temperature, and on cooling may condense in long ducts leading to the stack or in the stack itself. If no mist controls are employed or if the cooling occurs after the mist eliminator, the condensed vapor can be carried out of the stack as relatively large droplets which fall in the vicinity of the plant. Acid vapor may be reduced by operating the absorber at lower temperatures where H_2SO_4 vapor pressure is lower; however, this may increase acid mist formation.

Table 4.1 shows that the H_2SO_4 vapor pressure is dependent upon temperature and, to some extent, upon acid concentration (4). To reduce acid vapor emissions from a specific absorber, the lowest operating temperature consistent with good operation must be found. This generally lies in the range 170 - 185°F.

4.2.2 Sulfur Trioxide Vapor

If significant gaseous SO_3 is present in the stack gas as a result of poor absorber operation, it will combine with water vapor in the atmosphere to produce a visible acid mist. The only way to prevent this mist formation is through proper absorber operation and design (5).

Table 4.1 shows that the vapor pressure of SO_3 increases rapidly above 99 percent acid concentration (4). Since SO_3 absorption efficiency drops off below 98 percent acid concentration, control of concentration in the range 98 - 99 percent is generally good practice.

Concentrations of SO_3 in the absorber exit gas will of necessity exceed the equilibrium concentrations given in Table 4.1. This is because no absorber of finite height can achieve SO_3 equilibrium between the acid entering the top of the tower and the tower top exit gas.

TABLE 4.1

H_2SO_4 AND SO_3 VAPOR PRESSURES AT SELECTED ACID TEMPERATURES AND CONCENTRATIONS

H_2SO_4 (mm Hg)

	ACID CONCENTRATION		
TEMPERATUPE (°F)	96%	98%	100%
194	.064	.079	.094
176	.032	.039	.046
158	.015	.018	.022

SO_3 (mm Hg)

	ACID CONCENTRATION			
TEMPERATURE (°F)	96%	98%	99%	100%
194	.0003	.0013	.0049	.510
176	.0001	.0005	.0020	.276
158	.00005	.0002	.0008	.145

4.2.3 Particulate Acid Mist

Acid mist is formed anywhere in a sulfuric acid plant where sulfuric acid vapor is cooled below the dewpoint corresponding to that particular acid vapor concentration; the original H_2SO_4 vapor can arise from acid vapor pressure, or from reaction of SO_3 with water vapor in the carrier gas stream. Once formed, this mist is extremely stable, is not readily separated or absorbed, and much of it passes through the absorber. The quantity and particle size distribution of acid mist are functions of the sulfur feedstock and the strength of the acid produced.

For a bright elemental sulfur plant, the only sources of water vapor are moisture in the sulfur and in the inlet air to the drying tower. The drying towers in most contact plants are able to dry the process gas to a moisture content of about 3 milligrams per standard cubic foot (mg/scf) (6). Theoretically, the 3 mg/scf of water vapor will form 16 mg/scf of sulfuric acid mist. Part of the mist is probably removed in the absorber, however.

When dark or contaminated sulfur is burned, hydrocarbon impurities present in the sulfur burn to produce water vapor. This in turn combines with SO_3 to form acid mist as the gas cools in the economizer or absorption tower. This mist formation may be accentuated by sudden chilling of the gas on cold surfaces, an effect sometimes produced by rain on the gas duct. Existing information indicates that this mist consists of 1 to 5 micron particles (7).

Another cause of mist formation is the presence of nitrogen oxides in the converted gas. Although the nitrogen oxides may result from fixation of atmospheric nitrogen in high temperature furnaces or from arcing of electrostatic precipitators in the purification section upstream of the drying tower in non-sulfur burning plants, they more commonly result from nitrogen compounds in the raw material used. Spent acids recycled from organic reactions are most likely to produce nitrogen oxides. Part of the mist formation undoubtedly results from oxidation of SO_2 by these nitrogen oxides (the chamber plant reactions) (8). It is also believed that nitric oxide (NO) reacts with SO_3 to form nitrosyl pyrosulfate, $(NO)_2 S_3O_7$; and that nitrosyl pyrosulfate reacts with atmospheric moisture to form nitrosyl bisulfate, $NOHSO_4$. Nitrosyl pyrosulfate will pass through the final absorber and any mist eliminator in gaseous form at normal exit gas temperatures, and both nitrosyl pyrosulfate and nitrosyl bisulfate can exist in the stack gas as very fine mist. (9). These mist emissions can be minimized through use of high efficiency mist eliminators and/or electrostatic precipitators in the purification section and in the stack gas, and by proper furnace operation. As an example of the latter, one report claims that furnace operation below 2000°F with low oxygen content will insure that the decomposition products contain no more than 100 ppm of nitrogen oxides (8).

In "wet gas" plants burning hydrogen sulfide, no attempt is made to remove water vapor either from the combustion air or from the gas resulting from combustion of the hydrogen sulfide. Hence, the amount of water vapor in the gas entering the converter is more than enough to combine with all of the sulfur trioxide produced, and the entire output of the plant initially is in the form of acid mist. Most of this mist is recovered as product acid with gas cooling equipment and high efficiency mist eliminators.

In oleum producing plants, a greater quantity of mist and a much finer mist is produced. In these plants, oleum (i.e. sulfuric acid containing excess SO_3 in solution) is produced in a preliminary absorption step before the final absorption tower. Only part of the SO_3 is absorbed and the gas leaving the oleum tower still contains SO_3 which is absorbed in the final absorption tower. In spite of this preliminary absorption, the stack gas always contains more mist than when the oleum tower is bypassed. The quantity of mist appears to be proportional to the oleum/acid production ratio and to the strength of the oleum produced (10). The mechanism is not clearly understood but it has been established that the mist is formed in the final absorption tower, not in the oleum tower (7).

Table 4.2 gives a particle size distribution for sulfuric acid mist emissions at plants producing strong acid, 20 percent oleum and 32 percent oleum (11,12). These distributions were obtained using a cascade impactor (See Section 6.2.1.2 for a description). Table 4.2 indicates that oleum production results in a finer particle size distribution than acid production alone, and that the distribution becomes finer with increasing oleum concentration.

TABLE 4.2

PARTICLE SIZE DISTRIBUTIONS IN SELECTED SULFURIC ACID PLANT ABSORBER EFFLUENTS

Particle diameter (microns)	Cumulative weight percent smaller than		
	Acid production only	20% oleum production	32% oleum production
0.2	-	0.4	3.6
0.4	-	2	16
0.6	1	4.8	30
0.8	7	8	42
1.0	12	11.6	53
1.5	21	48	86.5
2.0	40	84.5	97

4.3 TYPICAL PLANT MIST EMISSIONS.

Figure 4.1 shows the relationship between mist concentration and pounds of mist per ton of acid produced. For a given mass emission rate, acid mist concentration (in milligrams of H_2SO_4 per standard cubic foot) is a function of the volume of air fed to the process. The air volume in turn depends on the SO_2 concentration in the gas stream fed to the converters. The curves can be used for any gas stream before or after mist eliminators, provided there is no air dilution.

Stack gas acid mist emissions range from 2 to 20 milligrams per standard cubic foot (mg/scf) for a plant producing no oleum to 5 to 50 mg/scf for an oleum plant (13). For a typical sulfur-burning system feeding 8 percent SO_2 to the converter, these stack gas emissions are equivalent to 0.4 to 4 pounds per ton (lb/ton) of 100 percent H_2SO_4 produced for an acid plant and 1 to 10 lb/ton of 100 percent H_2SO_4 produced for an oleum plant (refer to Figure 4.1). The lower mist limit in each range requires some form of mist control device while the upper limit is typical of no control.

Generally speaking, the dual absorption process does not reduce the acid mist emission, and a dual absorption plant will require the same type of mist control device as a conventional plant (14). An additional mist eliminator is required on the primary absorption

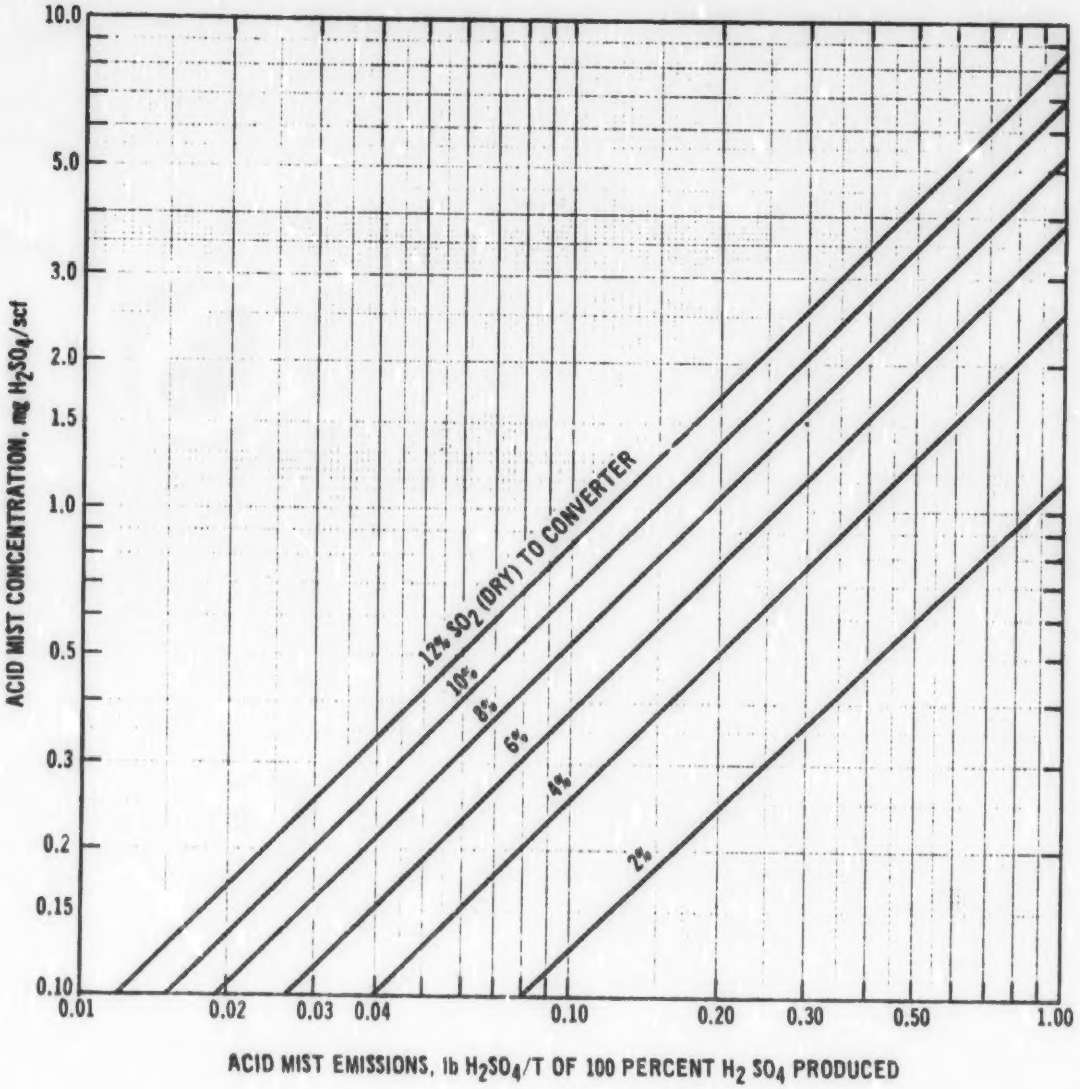

Figure 4.1 Sulfuric acid plant concentrations of mist for mass stack emissions per unit of production at inlet SO_2 volume concentrations.

tower (see Section 3.1.3) to protect the downstream heat exchangers from corrosion. This additional mist eliminator will often allow a less efficient mist eliminator (refer to Sections 6.2.1.2 and 6.2.1.3) to do an adequate final cleanup on the secondary absorption tower, whereas a high efficiency mist eliminator (Section 6.2.1.1) might otherwise have been required.

The use of a tail gas scrubbing system, for removal of SO_2, such as sodium sulfite or ammonia scrubbing, does not reduce the need for a mist eliminator since - as mentioned in Section 4.2 - acid mist is not readily absorbed.

With the sodium sulfite system, it is best to locate the mist eliminator upstream of the scrubber to minimize the formation of sulfates which must be purged from the system. It may even be desirable to have two high-efficiency mist eliminators: one installed in the absorber and the other "at grade", downstream of the absorber and upstream of the scrubber. ("At grade" and "piggyback" installations are discussed in Section 6.2.2). The scrubber exit gas does not normally require mist removal.

The ammonia solution scrubbing process requires a pH of 6.0 or greater for effective SO_2 control. However, as the pH of the liquor increases, ammonia losses increase and the ammonia combines with the SO_2 to form a highly visible plume of ammonium sulfite, bisulfite, and sulfate. A high efficiency mist eliminator must be installed downstream of the scrubber to control these emissions. Further information on the use of mist eliminators in ammonia solution scrubbing systems can be found in reference (15).

The use of a molecular sieve requires removal of all H_2SO_4 mist, H_2SO_4 vapor, and gaseous SO_3 upstream of the sieve, as H_2SO_4 cannot be regenerated from the sieve. This, and the fact that the sieve has a higher capacity at lower temperatures, requires that the absorber tail gas first be cooled by passage through a refrigeration system before passage through a high efficiency mist eliminator. This cooling cannot be achieved by water injection since the sieve absorbs water vapor. It cannot be achieved by lowering the acid temperature to the absorber as this may increase acid mist formation. A plant may choose to install another mist eliminator upstream of the cooler to reduce the load on the second mist eliminator. This mist eliminator would usually be installed in the absorber in new plants and "piggyback" or "at grade" in existing plants. Due to the extensive preliminary treatment, sieve stack gas should contain virtually no acid mist.

4.4 REFERENCES FOR SECTION 4.

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5. HEALTH AND WELFARE EFFECTS OF ACID MIST

5.1 INTRODUCTION

In accordance with 40 CFR 60.22(b), promulgated on November 17, 1975 (40 FR 53340), this chapter presents a summary of the available information on the potential health and welfare effects of sulfuric acid mist and the rationale for the Administrator's determination that it is a health-related pollutant for purposes of section 111(d) of the Clean Air Act.

The Administrator first considers potential health and welfare effects of a designated pollutant in connection with the establishment of standards of performance for new sources of that pollutant under section 111(b) of the Act. Before such standards may be established, the Administrator must find that the pollutant in question "may contribute significantly to air pollution which causes or contributes to the endangerment of public health or welfare"(see section 111(b)(1)(A)). Because this finding is, in effect, a prerequisite to the same pollutant being identified as a designated pollutant under section 111(d), all designated pollutants will have been found to have potential adverse effects on public health, public welfare, or both.

As discussed in section 1.1 above, Subpart B of Part 60 distinguishes between designated pollutants that may cause or contribute to endangerment of public health (referred to as "health-related pollutants") and those for which adverse effects on public health have not been demonstrated ("welfare-related pollutants"). In general, the significance of the distinction is that States have more flexibility in establishing plans for the control of welfare-related pollutants than is provided for plans involving health-related pollutants.

In determining whether a designated pollutant is health-related or welfare-related for purposes of section 111(d), the Administrator considers such factors as: (1) Known and suspected effects of the pollutant on public health and welfare; (2) potential ambient concentrations of the pollutant; (3) generation of any secondary pollutants for which the designated pollutant may be a precursor; (4) any synergistic effect with other pollutants; and (5) potential effects from accumulation in the environment (e.g., soil, water and food chains).

It should be noted that the Administrator's determination whether a designated pollutant is health-related or welfare-related for purposes of section 111(d) does not affect the degree of control represented by EPA's emission guidelines. For reasons discussed in the preamble to Subpart B, EPA's emission guidelines (like standards of performance for new sources under section 111(b) are based on the degree of control achievable with the best adequately demonstrated control systems (considering costs), rather than on direct protection of public health or welfare. This is true whether a particular designated pollutant has been found to be health-related or welfare-related. Thus, the only consequence of that finding is the degree of flexibility that will be available to the States in establishing plans for control of the pollutant, as indicated above.

5.2 HEALTH EFFECTS

Short-term human exposure to sulfuric acid mist can cause temporary and permanent damage to the lungs and bronchial tubes. Long-term exposure can cause skin damage, inflamation of the eyes, mouth and stomach, and permanent tooth damage, the latter being the most serious (1,2).

One hour exposure to a concentration of 39,000 micrograms per cubic meter ($\mu g/m^3$) of dry mist has produced persistent wheezing for up to 4 days after exposure, an increase in airway flow resistance of 35.5 to 100 percent above normal, and long-lasting bronchial irritation (3,4). A deep breath at a concentration of 5000 $\mu g/m^3$ will usually produce coughing. A concentration of 3000 $\mu g/m^3$ produces a noticeable odor, although concentrations below 600 $\mu g/m^3$ usually cannot be detected(1). Occupational exposure to 1000 $\mu g/m^3$ is unlikely to result in lung injury (2,5).

Workers exposed to long-term concentrations of 3000 to 16000 $\mu g/m^3$ evidenced severe corrosion of dental enamel (2,6), but no damage was noted after occupational exposure to 1000 $\mu g/m^3$ (2,7).

A threshold limit value of 1000 $\mu g/m^3$ for 8-hour workday exposure has been set by the American Conference of Governmental Industrial Hygienists, a level which should not cause irritation of respiratory passages and tooth injury (2). This same level was recommended by the National Institute for Occupational Safety and Health for occupational exposure to sulfuric acid mist as a time-weighted average exposure for up to 10 hours per day, 40 hour work week (10).

The effects of sulfuric acid mist on the lungs are aggravated by high humidity. In terms of sulfur equivalent, sulfuric acid is considerably more of an irritant to humans than is sulfur dioxide (2,4,39).

Emissions of the acids and oxides of sulfur contribute to the total sulfate concentration in the air. A method for measuring atmospheric H_2SO_4 is not available. A comparison of measured atmospheric sulfate with atmospheric metals and ammonium ions indicates that about half of the atmospheric sulfate could be in the form of H_2SO_4 (38). In 1970, the national average sulfate concentration at urban locations was 10.1 $\mu g/m^3$. The nonurban average was 6.3 $\mu g/m^3$ (37). Acid mist emissions add to the total background, but reliable no-effect threshold levels have not been established.

A recent investigation in guinea pigs demonstrated that the total respiratory deposition rate of inhaled particles and the pattern of regional respiratory deposition of these particles was altered by sulfuric acid mist inhalation. These effects were noted at acid mist concentrations as low as 30 $\mu g/m^3$, particle size < 1 μm, for 1 hour. This response was probably associated with increased pulmonary airflow resistance. Increased pulmonary airflow resistance is the principal physiologic response in uncomplicated asthma. It has been hypothesized, therefore, that sulfuric acid mist inhalation may act to increase the incidence of asthma attacks through increased deposition of inhaled particles and/or a shift in the principal site of desposition of inhaled particles to airway regions where asthma can be triggered (8).

Another recent animal study examined respiratory physiologic responses to a variety of sulfates of similar aerosol size and mass concentrations (9).

Sulfuric acid was found to be the greatest respiratory irritant. The differences in the inhalation response of some of these sulfates was small. Although these data do not constitute an adequate basis for a determination of the comparative toxicity for specific inorganic sulfates, the data do suggest that the toxicological evaluation of particulate sulfur oxides must consider the cation as well as the anion of the molecule, and that aerosol acidity is of great importance. These studies were based upon a sensitive respiratory physiologic response, primarily increased pulmonary airflow resistance in guinea pigs. This response results from narrowing of the airways within the respiratory system. A similar response has been observed in men exposed to sulfur dioxide and H_2SO_4 aerosol. This physiological response is a generally accepted, sensitive measure of airway irritation.

Data on sulfuric acid mist toxicity in humans are limited, but there is some information on short-term exposures. One study reported an increase in pulmonary flow resistance in humans of 18 percent at H_2SO_4 aerosol levels (particle size 1.8 μm, count median diameter) as low as 10 - 100 $\mu g/m^3$ (40), although the experimental techniques used in this study have been faulted by independent reviews.

In another study, respiratory rate has been reported to increase by about 30 percent, tidal volume to increase by about 28 percent, and maximum inspiratory-expiratory flow rates to decrease by about 20 percent at exposure levels of 350-500 $\mu g/m^3$, concentrations below subjectively detectable levels (5). These changes occurred during the first three minutes of exposure, were maintained throughout the 15 minute exposure period, and returned to pre-exposure levels within 15 minutes after the exposure ended. At higher levels, bronchospasm, increased upper respiratory tract secretions, increased flow resistance and increased respiratory rate have been consistently found. It thus appears that as H_2SO_4 concentration increases, so do respiratory rate and pulmonary air flow resistance. All of the subjects involved in the clinical studies were healthy, young adults who could easily compensate for the increased resistance imposed upon their breathing. Effects on persons with pre-existing disease have not been determined.

5.3 WELFARE EFFECTS

In addition to its effect on the bronchial tubes, another annoying property of sulfuric acid mist is the ability of the aerosol particles to reduce visibility. They do this by scattering and absorbing the light passing from object to observer thus reducing the eye's ability to distinguish objects from their background, and by scattering light from the sky and sun into the line of sight of an observer (12).

The most serious sulfuric mist visibility reduction is caused by small particles from 0.2 to 2 microns in diameter. About 5 to 20 percent of the particles in urban air are sulfuric acid and other sulfates, and 80 weight percent or more of these sulfate particles are smaller than 2 microns in diameter (13).

Visibility decreases with increasing acid mist concentration and increasing relative humidity, and is particularly important in aircraft operations. At a visual range of less than 5 miles, operations are slowed at airports because of the need to maintain larger distances between aircraft (13). Sulfuric acid mist can limit visibility to 5 miles at 98 percent relative humidity and an acid mist concentration of 200 $\mu g/m^3$, at 90 percent relative humidity, and 60 $\mu g/m^3$ and at 50 percent relative humidity and 200 $\mu g/m^3$ (14).

In atmospheres containing sulfur dioxide and sulfuric acid, an increase in humidity increases the ratio of sulfuric acid to sulfur dioxide and this results in an increase of sulfuric acid concentration in the size range characteristic of acid fogs (15).

Sulfuric acid mist exerts a negative economic effect by damaging materials and vegetation. Acid mist accelerates the corrosion of most metals, in particular iron, steel, and zinc. The damage increases with increasing relative humidity and temperature. In addition, atmospheric sulfuric acid can react with some suspended particulates to form sulfate salts which further accelerate the corrosion (16,17, 18,19,20).

Sulfuric acid will attack building materials and deface monuments. The attack is very severe if the building material contains calcium carbonate, as do limestone, marble, roofing slate, and mortar. The carbonate is converted to relatively soluble sulfates and then leached away by rainwater (21,22,23,24). Dolomites, which contain both calcium and magnesium carbonates, are particularly vulnerable as magnesium carbonate is readily soluble in an acid environment (21,25,26,27). Granite, gneiss, and many sandstones, which do not contain carbonates, and well-baked bricks, glazed bricks and glazed tile are less readily attacked by sulfuric acid. Sulfuric acid can also disintegrate stone structures by corroding iron tie rods (21,25).

Textile fabrics made of cellulosic vegetable fibers, such as cotton, linen, hemp, jute, rayons and synthetic nylons, are particularly vulnerable to sulfuric acid. After exposure, these fibers lose tensile strength (21,28). Animal fibers, such as wool and furs, are more resistant to acid damage (21,27). Certain classes of fabric dyes are attacked by sulfuric acid which is often absorbed or adsorbed on atmospheric particles. The dye coloring is reduced or sometimes destroyed entirely (21,29,30).

Sulfuric acid also causes discoloration, embrittlement, and a decrease in folding resistance of both book and writing paper (25,31,32).

Sulfuric acid droplets have settled on dry leaves without causing injury but when the leaf surface was wet, as may occur during polluted fogs, a spotted injury has developed. The injury consists of progressive cellular collapse from the exposed surface through the leaf leaving scorched areas (33,34,35). Injury may occur at concentrations of 100 $\mu g/m^3$ (36). Injury has occured on Swiss chard, beets, alfalfa and spinach, the latter showing a more diffuse type of injury (33).

5.4 RATIONALE

Based on the information in sections 5.2 and 5.3, it is clear that sulfuric acid mist has significant health and welfare effects. To be classified as a health related pollutant, the health effects of acid mist must be present at reasonably expected ambient concentrations. Results of diffusion modeling presented in section

8.1.1.2 indicate that expected maximum ground-level concentrations from uncontrolled acid and oleum plants are in the range of 0.6 to 12 μg/m^3 on an annual average, 3 to 60 μg/m^3 on a 24-hour average, 40 to 300 μg/m^3 on a one hour average, and 640 to 4700 μg/m^3 on a ten second average. (See Table 8.1 for complete results.)

The predicted short-term concentrations are in the range where health effects have been observed in healthy, young subjects (see section 5.2). It is a reasonable conclusion that potentially more sensitive individuals (e.g., infants and others of great susceptability such as persons whose health is already compromised by pre-existing disease conditions and whose physiologic reserves are, therefore, reduced) would exhibit adverse effects at even lower concentrations than the clinical studies indicated, or more serious adverse effects at the levels studied.

Therefore, the Administrator concludes that sulfuric acid mist contributes to endangerment of public health and may in fact cause that endangerment. Thus, sulfuric acid mist will be considered a health-related pollutant for purposes of section 111(d) and Subpart B of Part 60.

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6. CONTROL TECHNIQUES FOR ACID MIST

As mentioned in Section 1, the intent of the acid mist new source performance standard and these guidelines for existing facilities is to limit the H_2SO_4 concentrations in the atmosphere resulting from particulate acid mist, H_2SO_4 vapor, and gaseous SO_3. Acid mist is defined by EPA Method 8 which measures virtually all of the particulate acid mist, but only a fraction of the SO_3 and H_2SO_4 vapor.

Effective control of acid mist as defined in the standard thus requires more than control of particulate acid mist alone. As mentioned in Section 4.2, it also requires control of H_2SO_4 vapor and SO_3 through proper absorber operation. Consequently, Section 6.1 deals with absorber operating parameters that can affect the emission of H_2SO_4 vapor and SO_3; and Section 6.2 deals with control techniques for particulate acid mist.

Section 6.3 presents the results of EPA source tests to support the standard of performance for new stationary sources (SPNSS) for acid mist, EPA source tests to support this 111(d) document dealing with retrofit plants, and miscellaneous company-run source tests. All of the plants for which data are given were tested using EPA Method 8.

Section 6.4 presents EPA's emission guideline for existing sources based on applying the best system of emission reduction--considering cost--that is available to existing plants. This guideline reflects the application of the vertical panel or horizontal dual pad mist eliminators, as a minimum, to sulfur burning plants producing acid or low strength oleum, and generally require the application of vertical tube mist eliminators to other non-metallurgical sulfuric acid plants.

Section 6.5 deals with good plant operating practices that can reduce the generation of particulate acid mist upstream of the absorber.

6.1 ABSORBER OPERATION. (1,2)

In an absorption process, a soluble component of a gas mixture is dissolved into a relatively nonvolatile liquid. As the component is dissolved, it may react chemically with the liquid, with evolution or absorption of heat. Furthermore, if the gas and liquid enter the absorber at different temperatures, ordinary heat transfer will also occur from one stream to the other.

The final operation in a contact process sulfuric acid unit is the absorption of gaseous SO_3 into a liquid stream of strong H_2SO_4. The SO_3 is absorbed from a gas stream which also contains nitrogen, oxygen, SO_2, and particulate acid mist. Absorption is carried out by passing the liquid H_2SO_4 and the gas streams countercurrent to each other in a vertical packed cylindrical tower known as an absorber. The liquid H_2SO_4 drains down the packing by gravity and the gas flows upward through the tower, coming into intimate contact with the liquid on the surface of the packing. The gaseous SO_3 diffuses out of the gas stream into the liquid H_2SO_4, reacts with the water in the acid stream to form more H_2SO_4, and releases heat. Water make-up is necessary to maintain constant acid concentration to the absorber. The operation of the absorber also involves the physical transfer of heat from the gas to the liquid. In a typical absorber, acid enters the tower at 180°F and cools the gas stream nearly to its own inlet temperature, from about 450°F. The heat generated in the absorber leaves with the acid stream, thus requiring acid cooling external to the absorber.

In a well-designed and operated absorber, sufficient contact time is provided between the gas and the liquid streams so that the gas leaving the absorber contains equilibrium vapor concentrations of the liquid and of the component being dissolved. These equilibrium concentrations are characterized by the vapor pressures of the liquid and the component at the liquid concentration and temperature entering the absorber.

Table 4.1 (Section 4.2) gives H_2SO_4 and SO_3 vapor pressures at selected acid temperatures and concentrations. The table shows a distinct increase in H_2SO_4 vapor pressure (acid volatility) with an increase in temperature, and emphasizes the importance of controlling the acid temperature to the absorber. As mentioned in Section 4.2, a good operating range is generally 170 - 185°F. The table also shows a rapid increase in the vapor pressure of SO_3 as the acid concentration exceeds 99 percent, and emphasizes the importance of controlling the acid strength so that the concentration does not approach that of an oleum (greater than 100 percent acid). Although not shown in the table, the vapor pressure of SO_3 over oleum is even higher than its vapor pressure over 100 percent H_2SO_4. Since SO_3 absorption efficiency drops off below 98 percent acid concentration, a good operating range is generally 98 - 99 percent.

Proper absorber operation requires limiting the liquid temperature and concentration rises across the tower, and this requires that the liquid flow be maintained above a minimum level. Ideas on proper absorber acid flowrate have changed over the years, but it appears that the minimum flow required is about 2 gallons per minute of acid per ton per day of 100 percent H_2SO_4 produced. Installation of a flowmeter indicating acid flowrate to the absorber is good operating practice.

Proper absorber operation also requires even cross-sectional distribution of the liquid from the top to the bottom of the tower packing so that the gas receives maximum contact time on the surface of the packing and does not channel past the liquid. This even distribution requires proper arrangement of the packing and proper liquid distribution at the top of the packing. A detailed discussion of tower internals can be found in references (3,4).

The condition of the distributor and the packing should be checked during scheduled downtimes. The acid distribution can be checked by running acid over the tower with no gas flow. Also, if the packing is dirty, the tower should be washed out with clean acid during the downtime.

6.2 FIBER MIST ELIMINATORS

Effective control of stack gas acid mist emissions can be achieved by fiber mist eliminators and by electrostatic precipitators. Although electrostatic precipitators are frequently used in the purification section of spent acid plants, there is no evidence that any have been installed to treat the stack gas of sulfuric acid plants in the last two years (5,6). This disuse is probably due primarily to their relatively large size and resultant high installation cost compared to fiber mist eliminators and to the high maintenance cost required to keep the units operating within proper tolerances in the acid environment which is corrosive to the mild steel equipment. Hence, although electrostatic precipitators do have the advantage of operating with a lower pressure drop than fiber mist eliminators (normally less than 1 inch of H_2O), attention in this document is concentrated on fiber mist eliminators.

Fiber mist eliminators utilize the mechanisms of impaction and interception to capture large to intermediate size acid mist particles and of Brownian movement to effectively collect low to submicron size particles. Fibers used may be chemically resistant glass or fluorocarbon. Fiber mist eliminators are available in three different configurations covering a range of efficiencies required for various plants having low to high acid mist loadings and coarse to fine mist particle sizes respectively. The three fiber mist eliminator configurations are:

(a) Vertical tubes

(b) Vertical panels

(c) Horizontal dual pads

6.2.1 Description

6.2.1.1 Vertical tubes (7,8,9,10)

Tubular mist eliminators consist of a number of vertically oriented tubular fiber elements installed in parallel in the top of the absorber on new acid plants and usually installed in a separate tank above or beside the absorber on existing plants. Each element (see Figure 6.1) consists of glass fibers packed between two concentric 316 stainless steel screens. In an absorber installation, the bottom end cover of the element is equipped with a liquid seal pot to prevent gas bypassing. A pool of acid provides the seal in the separate tank design. Mist particles collected on the surface of the fibers become a part of the liquid film which wets the fibers. The liquid film is moved horizontally through the fiber beds by the gas drag and is moved downward by gravity. The liquid overflows the seal pot continuously, returning to the process.

Tubular mist eliminators use inertial impaction to collect larger particles (normally greater than 3 microns) and use direct interception and Brownian movement to collect smaller particles. The low superficial velocity of gas passing through the fiber bed--20 to 40 feet per minute--provides sufficient residence time for nearly all of the small particles with random Brownian movement to contact the wet fibers, effecting removal from the gas stream. The probability that such a particle could pass through the bed

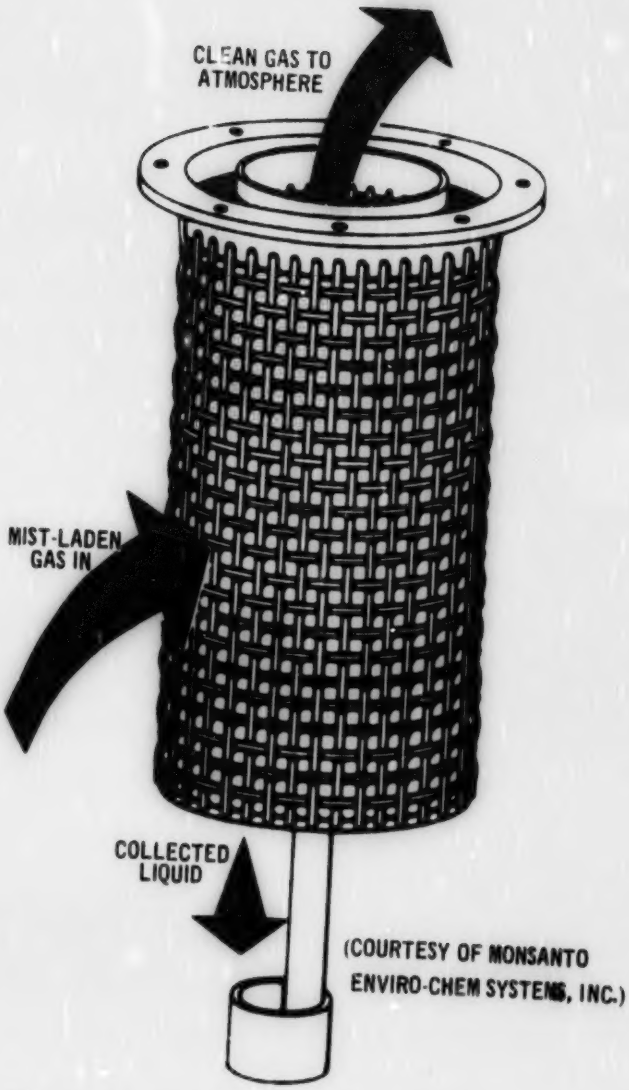

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Figure 6.1. Vertical tube mist eliminator element.

following the resultant greatly lengthened travel path is very low.

Design volumetric flow rate through an element is about 1000 standard cubic feet per minute (scfm) (11) and the number of elements required for a given plant size can be determined from the scfm handled at capacity. Depending on the size of the sulfuric acid plant, anywhere from 10 to 100 elements may be used; each element is normally 2 feet in diameter and 10 feet high (11).

Pressure drop across the element varies from 5 to 15 inches of H_2O with a higher pressure drop required for a higher removal efficiency on particles smaller than 3 microns. The manufacturer of these elements guarantees a mist removal efficiency of 100 percent on particles larger than 3 microns and 90 to 99.8 percent on particles smaller than 3 microns with 99.3 percent being most common (11). These efficiencies can be achieved on the stack gas of sulfuric acid plants burning elemental sulfur or bound-sulfur feedstocks (spent acid, wet gas, etc.) and producing acid or oleum.

Because the vertical tube mist eliminator does not depend only upon impaction for mist removal, it can be turned down (operated at a volumetric flow rate considerably below design) with no loss in efficiency.

6.2.1.2 Vertical panels (7,8,9,10,12)

Panel mist eliminators use fiber panel elements mounted in a polygon framework closed at the bottom by a slightly conical drain pan equipped with an acid seal pot to prevent gas bypassing. The polygon top is surmounted by a circular ring which is usually installed in the absorption tower and welded to the inside of the absorption tower head. Each panel element consists of glass fibers packed between two flat parallel 316 stainless steel screens (see Figure 6.2). In large high velocity towers, recent designs have incorporated double polygons, one inside the other, to obtain more bed area in a given tower cross section.

As in the high efficiency tubular mist eliminator above, the gas flows horizontally through the bed, but at a much higher superficial velocity (400 to 500 feet per minute) using the impaction mechanism for collection of the mist particles. Gas leaving the bed flows upward to the exit port while the collected liquid drains downward across the pan and out through the seal pot back into the tower or to a separate drain system.

The polygon may contain 10 to 48 vertical sides, each side normally consisting of an 18 1/2" x 53" panel. A smaller 18 1/2" x 26" panel is available for small plants, e.g., 35 tons per day (11).

Pressure drop across the panel is usually about 8 inches of H_2O. The manufacturer of panel mist eliminators will usually guarantee an emission no higher than 2 milligrams per cubic foot (equivalent to 0.375 pounds per ton of 100 percent H_2SO_4 produced -- see Figure 4.1) for a sulfur-burning plant producing oleum up to 20 percent in strength and/or acid (9,11). For an inlet loading of 20 milligrams per cubic foot which is typical of a plant not producing oleum (refer to Section 4.3), 2 milligrams per cubic foot outlet loading corresponds to a 90 percent removal efficiency.

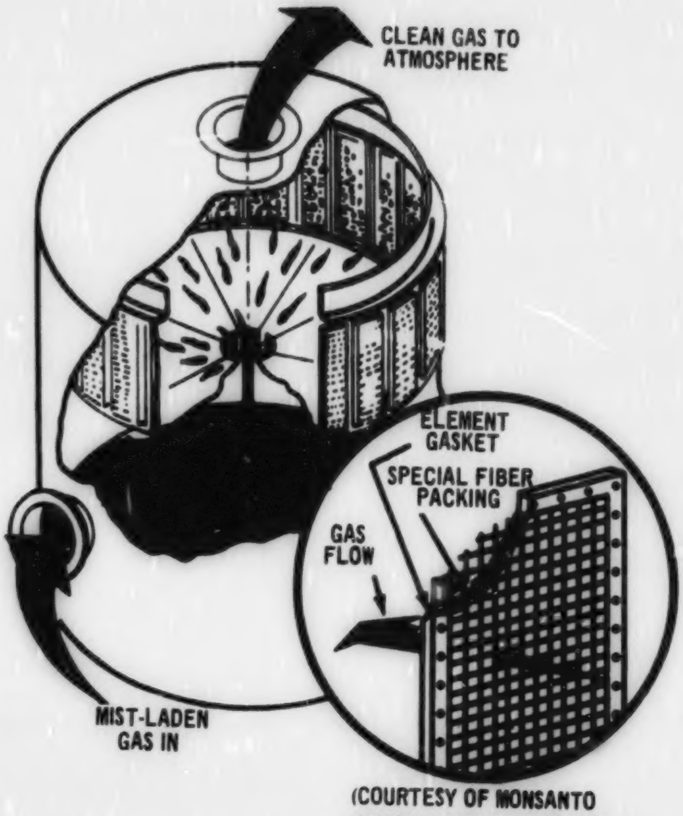

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Figure 6.2. Vertical panel mist eliminator.

Before guaranteeing that the above emission level will be met, it is necessary to obtain an acid mist particle size distribution curve on the absorber tail gas. This is done by sampling with a cascade impactor. Use of one such impactor available on the market is described in Industrial and Engineering Chemistry (13). The impactor separates the mist particles into several size fractions by passage in series through several impaction jets designed to collect progressively smaller particles. From these fractions, a particle size distribution curve can be constructed. The collection efficiency of the panel mist eliminator falls off below 1 micron. From the particle size distribution curve, the mist eliminator removal efficiency curve, and the acid mist loading, the expected acid mist emission from the panel mist eliminator can be calculated. Sampling with an impactor and calculating the particle size distributions can be time-consuming operations. However, the problem of guaranteeing an emission level is of more concern to a vendor than it is to EPA or to a State agency.

Because of the large percentage of submicron (below 1 micron) mist present in the stack gas of a spent acid plant and of a plant producing oleum stronger than 20 percent, the vertical panel mist eliminator will usually give unsatisfactory performance for these plants. (See Table 4.2 for oleum plant particle size distributions.)

Removal efficiency decreases as the gas velocity through the vertical panel mist eliminator drops below the lower design limit. This limit varies from unit to unit, the design limit being dependent upon many factors including local ordinances. As the velocity is lowered below this limit, acid mist emissions and the stack opacity increase. Hence, to properly enforce a standard, a State agency should measure the stack gas acid mist loading with the unit running at or near rated capacity, and not during unit startup or shutdown.

Vertical panel mist eliminators normally operate with a liquid level in the acid seal pot below the conical drain pan. Although the velocity through the panels could be increased at lower throughputs by raising the liquid level to cover the lower part of each panel, this would not be good practice since it would cause re-entrainment of spray by the gas passing over the liquid level in the basket.

Vertical panel mist eliminators also have an upper velocity design limit above which acid spray re-entrains from the inner surface of the polygon. This spray may or may not reach the atmosphere, depending upon the configuration of the ductwork. If it does, it normally will not cause an increase in stack opacity and will fall out on the plant equipment. Hence, operating above the upper limit should be of more concern to the plant operator than to EPA or a State agency. Further information on removal efficiency is contained in references (10,12).

6.2.1.3 Horizontal dual pads (7,14)

Two circular fluorocarbon fiber beds held by stainless steel screens are oriented horizontally in a vertical cylindrical vessel one above the other, so that the coarse fraction of the acid mist is removed by the first pad (bottom contactor--see Figure 6.3) and

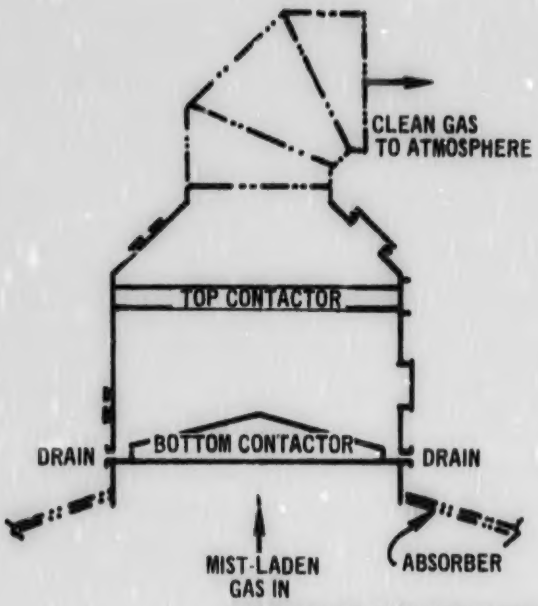

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Figure 6.3. Horizontal dual pad mist eliminator.

the fine fraction by the other (top contactor). The bottom contactor consists of two plane segmented sections installed at an angle to the horizontal to facilitate drainage and give additional area for gas contact. The assembly may be located adjacent to--or positioned on--an absorption tower.

This unit uses the high velocity impaction mist collection mechanism, as does the panel mist eliminator; however, the collected acid drains downward through the pads countercurrent to the gas flow producing a scrubbing action as well. Collected acid may be drained from external connections or returned directly to the absorber through liquid seal traps.

Total pressure drop across both pads is usually about 9 inches of H_2O. The superficial velocity through the unit is 9 to 10 feet per second. Hence, the diameter of the cylindrical shell and the pads is determined from the volume of gas handled. In one application, a 9-foot diameter unit was installed to handle 34,000 actual cubic feet per minute (acfm) at 160°F, and in another application an 11-foot diameter unit was installed to handle 51,000 acfm at 175°F. Height requirements for the unit depend upon whether it is located adjacent to or positioned on the absorber, but are roughly 1 1/2 to 2 times the diameter of the unit.

As with the panel mist eliminator, the dual pad unit will reduce acid mist emissions to 2 milligrams per cubic foot (0.375 pounds per ton of 100 percent H_2SO_4) or less, provided the plant burns sulfur and does not produce oleum stronger than 20 percent (14) and provided that a particle size distribution curve shows that this level can be met. (See Section 6.2.1.2 for a discussion of how a particle size distribution curve is obtained).

The removal efficiency of the horizontal dual pad mist eliminator decreases below the lower velocity design limit as it does for the vertical panel mist eliminator. When properly designed and installed, no increase in visible emissions should result from reducing the superficial velocity to 5 feet per second. However, just as with the vertical panel mist eliminator, it would be desirable for a State agency to measure the acid mist loading with the unit running near rated capacity, and not during unit startup or shutdown.

If a plant plans to run considerably below capacity for an extended period of time, it is possible to blank off some of the segments of the bottom contactor to maintain the desired removal efficiency.

Above a superficial velocity of 12 feet per second, the top contactor will not drain properly and the result is the same as for the vertical panel mist eliminator. Further information on removal efficiency is contained in reference (14).

6.2.2 Installation and Maintenance

6.2.2.1 Vertical tubes (11)

Figure 6.4 shows the installation of vertical tube elements in a separate tank ("at grade") which is the usual case for existing plants. The elements are bolted into a tube sheet supported by I-beam stiffeners and provided with a liquid seal to prevent gas bypassing. The tube sheet is one-inch carbon steel, and the tank is carbon steel above the tube sheet and carbon steel lined with acid-proof brick below the tube sheet. The vessel must have both sufficient space above the tube sheet and a large enough manway to allow positioning the elements. Representative tank sizes are 10'9" diameter x 23'5" for a 250 ton per day plant and 21'6" diameter x 25'3" for a 1000 ton per day plant.

The weight of the internals is determined by calculating the number of elements required and using a factor of 850-900 pounds for the unit weight of one element and its associated tube sheet when wetted with acid. The ducts leading to and from the tank are carbon steel, the inlet duct being sized for an average velocity of 1500-2000 fpm and the stack for 2000-4000 fpm. A new sump and pump is usually required to transport the collected acid to a storage tank.

If space is available, the elements can be installed in the final absorber. It is more common to install them in a "piggyback" unit mounted above the absorber on separate footings (10). These arrangements eliminate the sump and pump and minimize the ductwork.

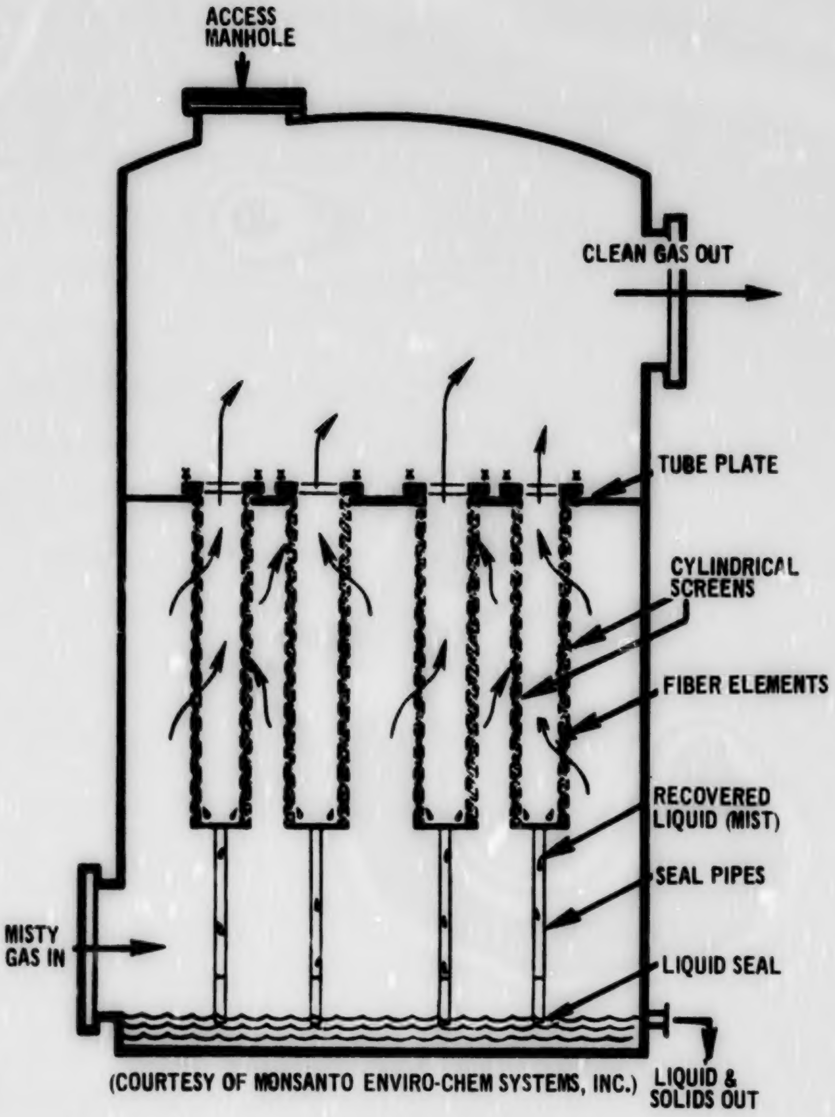

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Figure 6.4. Vertical tube mist eliminator installation.

Acid plants are usually designed with 20-30 inches of H_2O unused pressure drop out of a total of about 140 inches of H_2O plant pressure drop. However, as the unit becomes dirty this safety factor is used up. In order to insure no drop in production in a controlled plant, an additional fan to pull 25 inches of H_2O should be installed in series with the existing blower, unless a sufficient design allowance has been included in the total plant drop.

According to the manufacturer, tubular mist eliminators have been operating maintenance-free.

6.2.2.2 Vertical panels (11)

Figure 6.5 shows the installation of a vertical panel polygon in the top of the absorber, which is the usual case for existing plants. The polygon is constructed of 316 stainless steel and the top of the carbon steel tower is lined with acid-proof brick up to the dished head. About eight feet of vessel height are required to install the polygon. It is normally installed by putting a new top on the existing absorber or by cutting slits in the top of the existing absorber, lowering the panels through the slits, and assembling the cone inside the vessel. If the vertical panel unit was installed in a separate vessel, representative tank sizes would be 8'0" diameter x 10'7" for a 250 ton per day plant and 19'0" diameter x 13'7" for a 1000 ton per day plant.

Comments on stack velocity and on pressure drop in Section 6.2.2.1 also apply to the vertical panel installation.

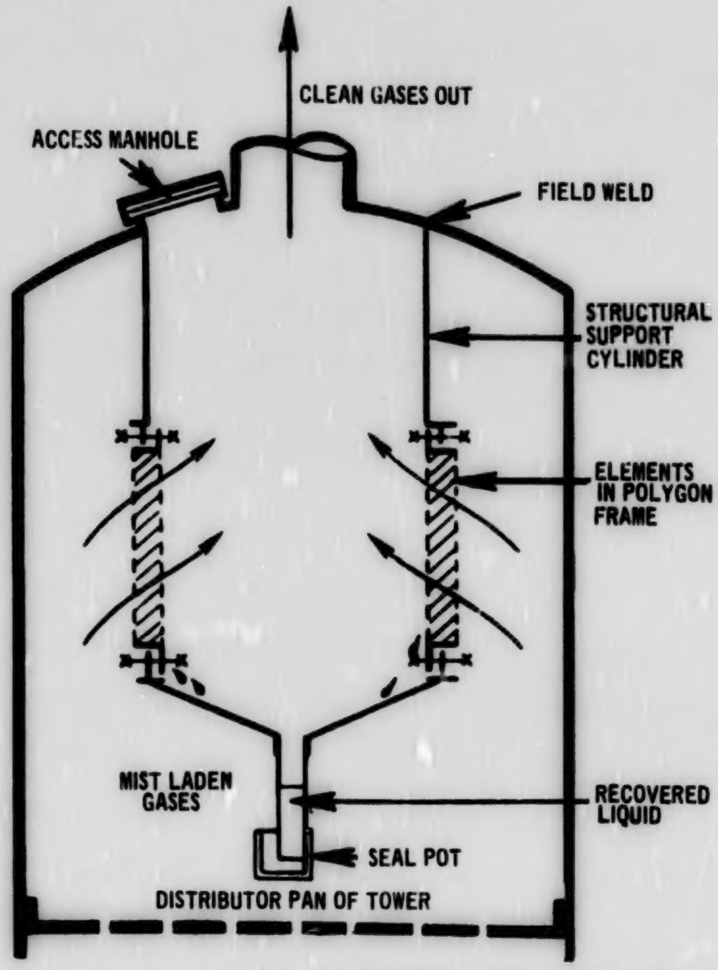

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Figure 6.5. Vertical panel mist eliminator installation.

Vertical panel mist eliminators are subject to corrosion of the wires holding the fibers in place in the panel by the high velocity acid flow. The panels have to be rescreened every six to seven years at a cost of 15-20 percent of the original equipment price of the unit. The corrosion is particularly severe on the bottom of the inside of the polygon.

6.2.2.3 Horizontal dual pads

Figure 6.6 shows a specific retrofit installation of a horizontal dual pad unit handling 34,000 acfm in the tail gas of an existing plant producing about 400 tons per day of 100 percent H_2SO_4. In this case (the 9-foot diameter unit discussed in Section 6.2.1.3) the unit is offset from the stack on the final absorber to prevent sulfate fouling of the pads by corrosion products formed in the stack (primarily iron sulfate). The unit is positioned on top of the adjacent drying tower (no process connection) and acid collected on the pad is drained through two one-inch drains to the drying tower.

The internal structural supports and ductwork for this installation are 304 low carbon stainless steel, as are the screens for the fiber beds. Stack and duct sizes for this installation are shown in Figure 6.6.

The comment on pressure drop in Section 6.2.2.1 also generally applies to a dual pad installation.

As mentioned above, dual pad mist eliminators are vulnerable to sulfate fouling. This fouling can be particularly severe when the plant is shut down. When the process gas flow is turned off, sulfate which has been held up in the stack can drain onto the

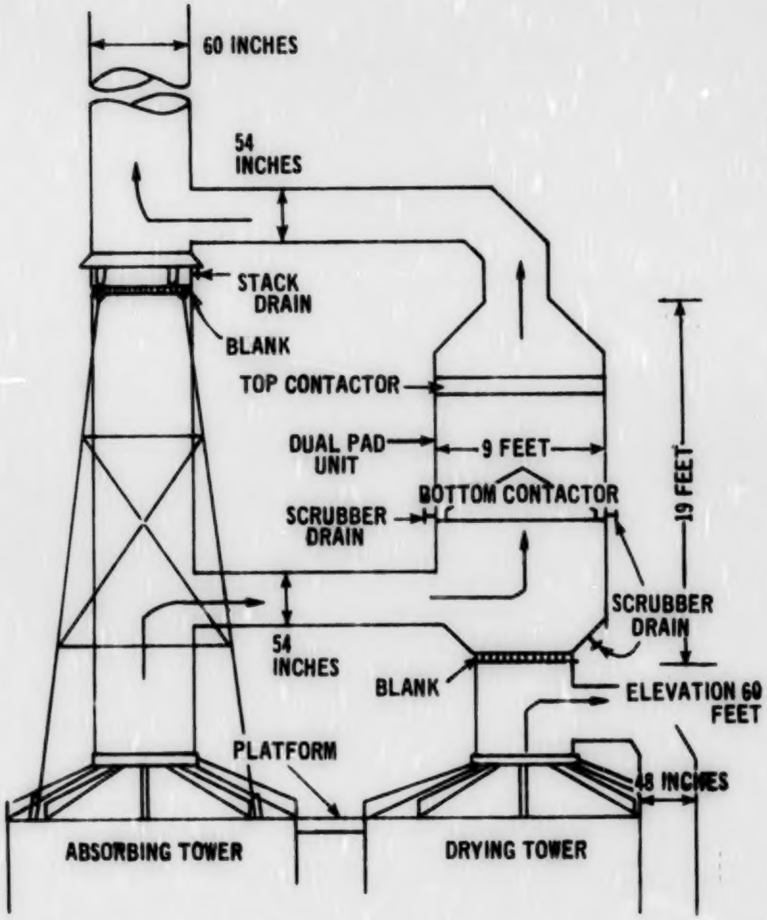

Figure 6.6. Retrofit horizontal dual pad mist eliminator installation.

pads. Dual pad mist eliminators are also subject to corrosion of the wires holding the fibers in place.

6.2.3 Design, Installation and Start-up Times

Table 6.1 presents manufacturers' May 1974 estimates of the normal length of time required to design and install fiber mist eliminators and bring the retrofitted unit back to normal operation (15,16). It shows that the total lead time required can vary from seven or eight months up to a year and a half.

The two items in Table 6.1 with the longest and most widely varying lead times are "Initial Design and Approval" and "Fabrication". Initial Design and Approval includes (15):

1) Engineering design of the overall layout including general specifications and drawings of the mist eliminator, tank and ductwork.
2) Project fund approval.
3) Control agency approval.
4) Order placement.

The above are all items over which the mist eliminator manufacturer has little control.

The lead time for fabricating vertical tube and vertical panel mist eliminators depends greatly upon the size of the order, the manufacturer's shop backlog, and the availability of steel for tank fabrication. The fabrication lead times shown in Table 6.1 are for tank fabrication; mist eliminator fabrication lead times

TABLE 6.1

MIST ELIMINATOR LEAD TIMES

(weeks)

	Vertical Tube and Vertical Panel	Horizontal Dual Pad
Initial Design and Approval	8 - 26	4 - 20
Preparation of Drawings	4 - 8	2 - 6
Plant Approval	3	3
Fabrication	13 - 35	30 - 45
Shipment	2	2
Installation	1 - 3	1
Startup	1	1
Totals	32 - 78	43 - 78

vary from 3-6 months (13-26 weeks). Tank fabrication lead times were no longer than 5 months (22 weeks) from 1960 to 1972, but increased dramatically from 1972 to 1974. Although 316 stainless steel is the normal material of contruction for vertical tube and vertical panel mist eliminators, a plant may occasionally require alloy 20 construction. In this case, the long delivery times on alloy 20 can make the mist eliminator fabrication lead time as long as a year (15). The long lead time for fabricating horizontal dual pad mist eliminators is due to long delivery times on steel. In 1973, fabrication took but 16-20 weeks (16).

The installation lead times in Table 6.1 assume that the mist eliminator can be tied-in as soon as it is delivered to the plant. To minimize production downtime, this delivery is generally scheduled to coincide with a planned unit shutdown (16).

Startup after a planned shutdown or after a shutdown specifically for tie-in usually takes a week or less. This does not include the time to test for compliance which usually adds another week to the total lead time. It is desirable to test for compliance with the acid unit running at capacity.

6.2.4 Costs

Table 6.2 summarizes the estimated costs for control of acid mist from existing acid plants. For each control unit and each type of installation, the installed capital cost, the net annual cost, and the net annual cost per ton of production (unit cost) are given for several sizes of acid plants as of November 1974.

Depending on the physical considerations of a particular plant, the control unit may be installed on top of the existing absorber or on the ground in an available space and connected by ducts to the absorber and the stack. The former is termed the "piggyback" installation, and the latter the "at grade" installation.

For cost estimation purposes, the piggyback horizontal dual pad installation is assumed to consist of dual pads pre-mounted inside a stainless steel vessel, which is installed on top of the existing absorber. The other two mist eliminator piggyback installations involve an extension of the acid-resistant brick-lined carbon steel absorber with the appropriate mist eliminator mounted inside. It is assumed that the piggyback installations require no additional supporting structure and that no additional fan capacity is added in order to arrive at a least-cost case.

The at grade installation houses the same type of control equipment mounted on a new foundation on the ground near the absorber. The cost of these installations is based on a new foundation, an acid return pump, additional ducting, and 25 inches of H_2O additional fan capacity.

TABLE 6.2

ACID MIST CONTROL COSTS FOR EXISTING SULFURIC ACID PLANTS

(1974)

Plant Size, TPD of 100% H_2SO_4	Piggyback Installation			
	50	250	750	1500
Gas Flow, acfm	3560	17,800	53,300	107,000
Horizontal Dual Pad				
Installed Capital Cost ($)	18,600	34,600	58,600	89,200
Net Annual Cost ($/year)	5,320-6,820	8,660-14,900	13,000-29,700	16,900-50,400
Unit Cost ($/ton)	0.32-0.42	0.11-0.18	0.05-0.12	0.03-0.10
Vertical Tube				
Installed Capital Cost ($)	60,000	160,500	345,000	557,500
Net Annual Cost ($/year)	15,100 - 16,600	40,400 - 46,700	87,700 - 105,000	141,000 - 175,000
Unit Cost ($/ton)	0.92 - 1.01	0.49 - 0.57	0.36 - 0.43	0.29 - 0.36
Vertical Panel				
Installed Capital Cost ($)	22,900	56,500	148,000	274,000
Net Annual Cost ($/year)	5,820-7,180	13,400-19,200	36,100-51,500	65,700-96,500
Unit Cost ($/ton)	0.35-0.44	0.16-0.23	0.15-0.21	0.13-0.20

TABLE 6.2 - PAGE 2

ACID MIST CONTROL COSTS FOR EXISTING SULFURIC ACID PLANTS

Plant Size, TPD of 100% H_2SO_4	At Grade Installation			
	50	250	750	1500
Gas Flow, acfm	3560	17,800	53,300	107,000
Horizontal Dual Pad				
Installed Capital Cost ($)	NA	NA	NA	NA
Net Annual Cost ($)				
Unit Cost ($/ton)				
Vertical Tube				
Installed Capital Cost ($)	99,300	266,000	572,000	909,400
Net Annual Cost ($)	26,300-27,800	70,500-76,800	152,400-169,300	241,000-275,000
Unit Cost ($/ton)	1.60-1.69	0.86-0.94	0.62-0.69	0.49-0.56
Vertical Panel				
Installed Cost ($)	52,000	126,000	339,000	624,000
Net Annual Cost ($)	12,800-14,200	30,200-35,900	82,400-97,800	150,000-181,000
Unit Cost ($/ton)	0.78-0.36	0.37-0.44	0.33-0.40	0.31-0.37

The installed cost range between these two types of installations should be representative of the costs for most acid plants. However, there may be certain plants which could experience costs outside the range due to the variability in factors such as: additional structural support requirements, fan requirements, congestion at the plant site with difficulties in ducting, and design allowances built into the existing absorber for future installation of the control elements.

The installed cost for the horizontal dual pad installation shown in Figure 6.6 was $57,000 in early 1970. Multiplying by a cost index ratio of 1.5 gives an installed cost of $85,000 for November 1974. The unit handles 34,000 acfm and by linear interpolation of Table 6.2 would be expected to cost about $46,000 (in November 1974 dollars). The additional cost is at least partially due to the ductwork to and from the unit, the inclusion of three access platforms, added structural support, and labor costs above the national avergge.

The installed capital costs (Table 6.2) for the vertical tube unit are based on element capital costs for 99.3 percent removal efficiency on particles 3 microns and smaller in diameter at 12 inches of H_2O pressure drop. Figure 6.7 shows the relative element capital costs for designs at other combinations of removal efficiency and pressure drop.

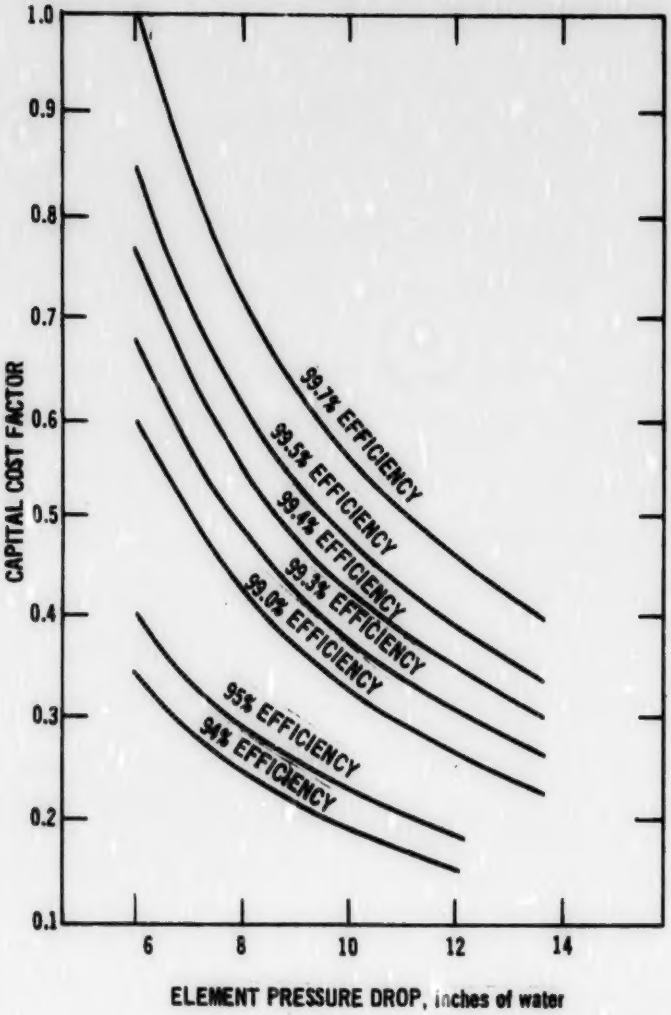

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Figure 6.7. Relative changes in capital costs for vertical tube mist eliminator elements at different removal efficiencies and pressure drops.

The gross annual cost consists of: capital related charges such as depreciation, interest on borrowed capital, property tax, insurance, and overhead which add up to 26 percent of the installed capital cost; operating cost which is totally made up of power cost for the pressure drop caused by the control unit; and maintenance cost which is based on information supplied by the equipment manufacturers. In order to determine the net annual cost, the credits for recovered acid are subtracted from the gross annual cost.

The wide range of reported emission rates for acid mist results in a range of cost credits and a range of net annual costs. The higher the pre-control emission rate, the higher the credit for recovered product would be. The value of the acid recovered is based on the production cost (see Table 6.4) rather than on the market sales price. The final figures shown in Table 6.2 are the net annual cost per ton of production. An operating ratio (production/capacity) of 90 percent is assumed for this calculation.

Table 6.3 shows the approximate installed capital cost for control of acid mist in new acid plants as of November 1974. They were obtained by multiplying the costs in Table 15, reference (7), by a cost index ratio of 1.58. The cost for a new plant should always be less than the cost for retrofit since the control unit can be designed in from the beginning (usually as an expanded section at the top of the absorber). The fact

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TABLE 6.3

INSTALLED CAPITAL COSTS FOR ACID MIST CONTROL IN NEW PLANTS

	Size (TPD of 100% H_2SO_4)			
	50	250	750	1500
Horizontal Dual Pad ($)	15,800	31,600	44,200	60,000
Vertical Tube ($)	87,400	111,000	166,000	269,000
Vertical Panel ($)	22,000	36,400	87,000	151,000

that this does not appear to be the case for the 50 TPD vertical tube piggyback installation is probably due to differences in cost estimating procedures.

To facilitate comparison of the above acid mist control costs to the total costs of installing and operating a sulfuric acid unit, Table 6.4 shows estimated capital cost and production cost for a new sulfur burning dual absorption unit as of November 1974. Accurate cost figures are not available to allow comparison with an existing unit. Costs are given for a dual absorption unit since all new units will have to be dual absorption or employ tail gas scrubbing systems to control SO_2 emissions to the level required in the EPA standard of performance for new sulfuric acid plants. Table 6.4 is based on information (17) used to support this new source standard. This information source cites capital

TABLE 6.4

ESTIMATED COSTS FOR NEW SULFUR BURNING DUAL ABSORPTION SULFURIC ACID UNIT

	Size (TPD of 100% H_2SO_4)			
	50	250	750	1500
Capital Cost ($)	903,000	2,650,000	5,539,000	8,810,000
Production Cost ($/Ton)	30.68	23.34	20.18	18.7

and production costs for a 1000 TPD acid plant. The capital costs for the sizes given in the table are extrapolated using an exponent of 0.67 from the Chemical Engineering cost file (18).

The production costs for the sizes given were determined from utility, raw material and labor requirements and capital charges for the same 1000 TPD plant cited above (17).

6.3 EMISSION REDUCTION

6.3.1 SPNSS Source Testing

Table 6.5 presents the results of testing performed during 1971 by EPA in developing the acid mist standard of performance for new stationary sources (SPNSS). All three plants tested employed vertical tube mist eliminators. All runs were made using EPA Method 8. All of the test results are equal to or less than the acid mist standard of performance for new sulfuric acid plants of 0.15 pounds per ton of 100 percent H_2SO_4 produced.

Unit A had a capacity of 700 tons per day (TPD) of 100 percent H_2SO_4 and burned only dark sulfur at the time of the test. It produced 35 percent oleum on February 17, and 30 percent oleum on February 18, but the oleum/acid production ratios are unknown. The unit was less than a year old at the time of this test, the mist eliminator being installed when the unit was built.

Unit B had a capacity of 750 TPD at the time of the test. On March 27, it burned 250 TPD of spent acid (on a 100 percent H_2SO_4 basis) and the balance was elemental sulfur. On that same day, it produced 70 TPD of 93 percent acid, 460 TPD of 98 percent acid, and 200 TPD of 20 percent oleum (all on a 100 percent H_2SO_4 basis). Unit B is an older unit whose mist eliminator had been retrofitted. Subsequent to this retrofit but prior to the EPA tests, a sodium sulfite scrubbing tower for SO_2 control was installed downstream of the mist eliminator. The tests were conducted downstream of this scrubbing tower.

TABLE 6.5

1971 ACID MIST TEST RESULTS USING EPA METHOD 8

Unit and Process	Mist Eliminator	Run No.	Date	Production Rate Tons/Day	Gas Flow SCFM (a)	Acid Mist mg/SCF	Acid Mist lbs/ton 100% H_2SO_4
A - Dual Absorption	Vertical Tube on Primary Absorption Tower and Vertical Panel on Final Absorption Tower	1	2/17/71	365	21,669	0.107	0.02
		2	2/18/71	360	16,226	0.535	0.08
		3	2/18/71	360	17,283	0.132	0.02
B - Single Absorption, Scrubber	Vertical Tube	1	3/27/71	730	35,141	0.279	0.04
		2	3/27/71	730	36,292	0.965	0.15
C - Single Absorption	Vertical Tube	1	8/31/71	185	20,737	0.244	0.09
		2	9/1/71	175	20,354	0.208	0.08
		3	9/1/71	175	20,958	0.200	0.08
		4(b)	9/2/71	193	20,506	0.202	0.07
		5(b)	9/2/71	193	20,549	0.207	0.07

(a) Five significant figures are retained here and in Table 6.6 for ease of identification against original data.

(b) Sampling without traversing at point of average velocity.

Unit C had a capacity of 450 TPD at the time of the test. During the period August 31 - September 2, it burned spent acid and sulfur and produced 20 percent oleum and 99 percent acid. The spent acid/sulfur feedstock ratios and the acid/oleum production ratios are unknown. However, average consumption for the months of August and September combined are 266 TPD of spent acid and 204 TPD of sulfur. For the same two-month period, average production was 242 TPD of acid and 210 TPD of oleum (all grades). All of the above rates are on a 100 percent H_2SO_4 basis. The total production and consumption rates of 452 and 470 TPD, respectively, indicate a unit conversion efficiency of about 96 percent. Unit C is an older unit with a very unusual design. The converter exit gas is split in half and fed to two equivalently-sized final absorbers. Each absorber is followed by a booster blower, a mist eliminator, and a stack. Both mist eliminators are retrofits. EPA tested one stack. The equivalent capacity for this one stack is thus 225 TPD. The production rates shown in Table 6.5 (186, 175, 193 TPD) also apply only to this stack and are one-half of the total unit production rates.

6.3.2 Section 111(d) Source Testing

Table 6.6 presents the results of additional testing performed under EPA supervision by a contractor. The purpose of these two tests was to define the performance of the vertical panel and the horizontal dual pad mist eliminators covered in this document, and to compare

TABLE 6.5

RESULTS OF ACID MIST TESTING FOR SECTION 111(d)

Unit and Process	Mist Eliminator	Run No.	Date	Production Rate Tons/Day	Gas Flow SCFM	Test Method	Acid Mist mg/SCF	Acid Mist lbs/ton 100% H_2SO_4
D - Single Absorption	Vertical Panel	1	11/14/72	1025	83,186	EPA 8	1.107	0.28
		2	11/15/72	1049	86,239	EPA 8	0.620	0.16
		3	11/15/72	1049	86,510	EPA 8	0.983	0.26
		4	11/15/72	1049	81,695	EPA 8	1.019	0.25
		5	11/16/72	1028	83,325	EPA 8	0.549	0.14
		6	11/16/72	1028	75,455	EPA 8	0.708	0.17
D - Single Absorption	Vertical Panel	1	11/14/72	1025	83,186	Monsanto	0.943	0.24
		2	11/15/72	1049	86,239	Monsanto	0.610	0.16
		3	11/15/72	1049	86,510	Monsanto	0.712	0.19
		4	11/15/72	1049	81,695	Monsanto	0.868	0.22
		5	11/16/72	1028	83,325	Monsanto	0.564	0.15
		6	11/16/72	1028	75,455	Monsanto	0.597	0.14

Note: All tests run by EPA-Contractor.

TABLE 6.6 - PAGE 2

Unit and Process	Mist Eliminator	Run No.	Date	Production Rate Tons/Day	Gas Flow SCFM	Test Method	Acid Mist mg/SCF	Acid Mist lbs/ton 100% H_2SO_4
E - Single Absorption	Horizontal Dual Pad	1	11/29/72	368	27,772	EPA 8	0.402	0.10
		2	11/29/72	368	29,413	EPA 8	0.265	0.07
		3	11/30/72	376	30,455	EPA 8	0.224	0.06
		4	11/30/72	376	29,304	EPA 8	0.192	0.05
		5	12/1/72	363	28,579	EPA 8	0.320	0.08
		6	12/1/72	363	28,503	EPA 8	0.194	0.05
E - Single Absorption	Horizontal Dual Pad	1	11/29/72	368	28,418	Monsanto	0.402	0.10
		2	11/29/72	368	28,613	Monsanto	0.366	0.09
		3	11/30/72	376	30,762	Monsanto	0.274	0.07
		4	11/30/72	376	30,232	Monsanto	0.326	0.08
		5	12/1/72	363	30,509	Monsanto	0.494	0.13
		6	12/1/72	363	29,710	Monsanto	0.292	0.08

Note: All tests run by EPA-Contractor.[7]

EPA Method 8 with the Monsanto Method by simultaneous runs with both methods[a]. The latter is important because considerable data based on the Monsanto Method exists.

Unit D had a capacity of 1100 TPD, burned moderately dark sulfur and produced 93 percent acid (no oleum) at the time of the test. The unit was then only about a year old, the vertical panel mist eliminator being installed when the unit was built. It would have been desirable to test an older unit that had been recently retrofitted with a vertical panel mist eliminator, but no assistance was obtained from the vendor in locating a suitable unit, and the unit tested was the most suitable one that could be found within the time available. The vertical panel mist eliminator tested was of the double polygon design. Further information on double polygons is contained in Section 6.2.1.2 and in reference (10). Gas leaving the absorber flowed through the two polygons in parallel, not in series, so that the performance of this design at Unit D should be identical to that which would have been obtained had the unit been equipped with a single polygon of equal cross-sectional bed area.

Unit E had a capacity of 350 TPD and also burned moderately dark sulfur and produced 93 percent acid (no oleum) at the time of the test.

(a) Mention of a trademarked product or company name is not intended to constitute endorsement by the Environmental Protection Agency.

It is an older unit that had been retrofitted with a horizontal dual pad mist eliminator in early 1970.

Testing of Units D and E with the EPA and Monsanto trains was done simultaneously so that, for instance, Unit D, Run Number 1, EPA Method was run at the same time as Unit D, Run Number 1, Monsanto Method. At Unit D, only one sampling port was available and consequently sampling was done across one diameter with the probes of the two trains adjacent. A velocity check across the diameter perpendicular to the test diameter indicated a similar flow pattern to that of the test diameter. At Unit E, sampling was conducted through two ports on perpendicular diameters. The probe of one train traversed the horizontal diameter for the first half of a run and the vertical diameter for the second half, while the probe of the other train traversed the vertical for the first half and the horizontal for the second half. The gas flows as measured are not identical for the individual EPA and Monsanto runs (Run 1 vs. Run 1) because separate velocity traverses were made for each train.

The EPA catch consisted of the probe, first impinger and filter. The Monsanto method used was as specified in references (19,20) and was not the modified Monsanto method. The Monsanto catch included the probe, cyclone, and filter. Inclusion of the probe catch is particularly important as it represented a significant fraction of the total catch for all the runs. Further process, sampling and analytical information on these two tests is contained in the source test reports (21, 22).

The EPA Method results averaged higher than the Monsanto Method results for Unit D, while for Unit E, the reverse was true. However, linear regression analysis of the data in Table 6.6, shows that the EPA and Monsanto methods are related by the equation:

$$\text{Conc.}_{\text{Monsanto}} = 0.63\ \text{Conc.}_{\text{EPA}} + 0.19$$

The coefficient of correlation is 0.97. Thus, although the two methods do not give identical results, the results of one method can be predicted from the results of the other method with a reasonable degree of accuracy for these particular sulfur burning plants controlled with pads or panels. It should be emphasized that these results were obtained from only two tests and that they do not mean that the two test methods used are necessarily equivalent for all acid plants.

It is important that the performance of both mist eliminators using both test methods was well below the 2.0 milligrams per cubic foot, actual or standard, that the manufacturers of these mist eliminators will guarantee. The results do not mean that the horizontal dual pad mist eliminator's performance is superior to the vertical panel's performance since the two mist eliminators were not tested under identical conditions. The results also do not mean that a sulfur-burning acid unit with a horizontal dual pad mist eliminator can consistently meet the new source performance standard of 0.15 pound per ton of 100 percent H_2SO_4 as it did in this test.

6.3.3 Miscellaneous Source Test Data

Table 6.7 presents the results of EPA Method 8 testing performed by companies and submitted to EPA and State air pollution control agencies. The data in Table 6.7 for plants A, I and J were voluntarily submitted in 1972 (plant A) and in October 1974 (plants I & J) to the EPA Research Triangle Park, N.C. offices by the respective companies. A considerable effort was made to obtain other EPA Method 8 test data. In October 1974, six EPA regional offices and 10 State agencies were contacted, and data were obtained for only three plants (F, G and H). There is no trade association specific to the sulfuric acid industry, and the Manufacturing Chemists Association had no data.

Unit A is the same Unit A that EPA tested (Section 6.3.1). It had a capacity of 700 TPD, burned elemental sulfur, and produced acid and oleum at the time of the company-run test. Oleum/acid production ratios and known oleum strengths are given in Table 6.7. The unit produced 30 percent oleum on December 9, 1971. Runs were made

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the probe, cyclone, and filter. Inclusion of the probe catch is particularly important as it represented a significant fraction of the total catch for all the runs. Further process, sampling and analytical information on these two tests is contained in the source test reports (21, 22).

The EPA Method results averaged higher than the Monsanto Method results for Unit D, while for Unit E, the reverse was true. However, linear regression analysis of the data in Table 6.6, shows that the EPA and Monsanto methods are related by the equation:

$$\text{Conc.}_{\text{Monsanto}} = 0.63\ \text{Conc.}_{\text{EPA}} + 0.19$$

The coefficient of correlation is 0.97. Thus, although the two methods do not give identical results, the results of one method can be predicted from the results of the other method with a reasonable degree of accuracy for these particular sulfur burning plants controlled with pads or panels. It should be emphasized that these results were obtained from only two tests and that they do not mean that the two test methods used are necessarily equivalent for all acid plants.

It is important that the performance of both mist eliminators using both test methods was well below the 2.0 milligrams per cubic foot, actual or standard, that the manufacturers of these mist eliminators will guarantee. The results do not mean that the horizontal dual pad mist eliminator's performance is superior to the vertical panel's performance since the two mist eliminators

TABLE 6.7

RESULTS OF ACID MIST TESTS MADE BY COMPANIES USING EPA METHOD 8

Unit	Process	Mist Eliminator	Run No.	Date	Feedstocks	Ratio: Bound Sulfur/Total Feed Sulfur(a)	Production Rate Tons/Day	Average Oleum Strength (% free SO_3)	Ratio:Oleum/Total Acid Production(b)	Acid Mist Lbs/Ton 100% H_2SO_4
A	Dual Absorption	Vertical Tube on Primary Absorption Tower and Vertical Panel on Final Absorption Tower	1(c)	12/8/71	Sulfur	-	700	N.A.(d)	0	0.07
			4	12/11/71	"	-	700	N.A.	0.16	0.01
			5	12/12/71	"	-	700	N.A.	0.08	0.11
			6	12/13/71	"	-	700	35	0.15	0.10
F	Dual Absorption	Vertical Tube on Primary Absorption Tower and Vertical Panel on Final Absorption Tower	1	2/19/74	Sulfur	-	1552	-	-	0.06
			2	2/19/74	"	-	1625	-	-	0.04
			3	2/20/74	"	-	1683	-	-	0.05
G	Single Absorption, Scrubber	Vertical Tube	1	7/74	H_2S	1.0	242	-	-	0.15
			2	7/74	"	1.0	251	-	-	0.21
			3	7/74	"	1.0	232	-	-	0.13
H	Single Absorption, Scrubber	Horizontal Dual Pad	9(e)	3/16/73	Sulfur	-	0.90(f)	30	0.36	0.20

TABLE 6.7 - PAGE 2

Unit	Process	Mist Eliminator	Run No.	Date	Feedstocks	Ratio: Bound Sulfur/Total Feed Sulfur[(a)]	Production Rate Tons/Day	Average Oleum Strength (% free SO_3)	Ratio: Oleum/ Total Acid Production[(b)]	Acid Mist Lbs/Ton 100% H_2SO_4
I	Single Absorption	Horizontal Dual Pad	1 (g)	5/72	Sulfur + Spent Acid	0.22	1.03	26	∿0.6	0.38
			2	5/72	"	0.21	1.07	26	∿0.6	0.24
			3	5/72	"	0.23	1.06	25	∿0.6	0.17
			4	6/72	"	0.19	1.04	25	∿0.6	0.28
			5	6/72	"	0.19	1.04	26	∿0.6	0.22
I	Single Absorption	Vertical Tube	2(e)	10/18/73	Sulfur + Spent Acid	0.21	0.94	28	0.70	0.26
			3	10/19/73	"	0.21	0.93	24	0.70	0.21
			4	10/20/73	"	0.21	0.93	24	0.70	0.46
J	Single Absorption	Vertical Tube	1	10/30/73	Ammonium Sulfate Waste + Sulfur	0.91	0.99	20	0.57	0.06
			2	10/31/73	"	0.91	0.89	20	0.57	0.06
			3	10/31/73	"	0.91	0.89	20	0.57	0.07

Footnotes:
(a) 100% H_2SO_4 produced from bound sulfur feedstocks ÷ total production on a 100% H_2SO_4 basis.
(b) Oleum produced expressed on a 100% H_2SO_4 basis ÷ total production on a 100% H_2SO_4 basis.
(c) Sampling difficulties during runs 2 and 3; test data invalid.
(d) Not available.
(e) Other runs were made using other test methods.
(f) This and succeeding values in this column are operating ratios (production/capacity).
(g) Run numbers assumed for these five runs.

using other test methods besides EPA Method 8 during the company-run test at Unit A, but no simultaneous runs involving EPA Method 8 and another test method were made.

Unit F had a capacity of 1525 TPD, burned elemental sulfur and did not produce oleum at the time of the test. Unit F was new at the time of the test, **the mist eliminators having been installed when the unit was built.**

Unit G had a capacity of 240 TPD, burned only hydrogen sulfide and did not produce oleum at the time of the test. This unit was also new at the time of testing, the mist eliminator having been installed when the unit was built.

Units H, I, and J all produced oleum during testing. Unit H burned sulfur; Unit I burned sulfur and spent acid; and unit J burned sulfur and waste acid containing ammonium sulfate. Bound sulfur/total sulfur feedstock ratios, operating ratios (production/capacity), oleum strengths and oleum/total acid production ratios are given in Table 6.7. For unit H, the mist eliminator was a retrofit installed upstream of an SO_2 tail gas scrubber. For unit I, the horizontal dual pad mist eliminator was replaced in 1973 with a vertical tube mist eliminator.

It is important that all of the data in Table 6.7 are below 0.5 pounds of mist per ton of 100 percent H_2SO_4 produced.

Table 6.8 gives particle size distributions in the gas streams entering and leaving a horizontal dual pad mist eliminator at one specific spent acid plant producing strong oleum (23). Each set of data is an average of five individual runs taken over the period February 10-25, 1972. The plant burned spent acid and sulfur during one of the five inlet sampling runs and three of the five exit sampling runs, and burned only elemental sulfur for the rest. It produced oleum during all the runs, in strengths varying from 23.4 to 27.5 percent free SO_3. Production of oleum approached 60 percent of total acid production.

The particle size distribution in Table 6.8 was determined using a cascade impactor. Further information on the cascade impactor is contained in Section 6.2.1.2 and reference (13). The average acid mist inlet loading for the five inlet runs was 3.81 mg/scf, and the average exit loading was 2.11 mg/scf corresponding to 0.37 lb/ton. This data was obtained using the Monsanto test method.

Table 6.8 shows that a significant percentage of the acid mist in the absorber effluent is submicron. The above inlet and exit loadings shows that impaction devices, such as the horizontal dual pad mist eliminator, do not effectively remove such mist.

6.3.4 Extent of Acid Mist Control

Accurate information on the number of units with controlled and uncontrolled stack gas is most difficult to obtain. The best

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TABLE 6.8

HORIZONTAL DUAL PAD MIST ELIMINATOR INLET AND EXIT PARTICLE SIZE DISTRIBUTIONS AT A SULFURIC ACID PLANT PRODUCING STRONG OLEUM (23)

Mist Eliminator Inlet		Mist Eliminator Exit	
Particle diameter (microns)	Cumulative weight percent smaller than	Particle diameter (microns)	Cumulative weight percent smaller than
0.4	33.9	0.4	43.9
0.7	41.8	0.7	50.7
1.3	73.2	1.4	65.8
1.9	81.0	2.0	72.5
3.2	82.7	3.1	76.8

information available to EPA is late 1972 data which show that about 40 percent of the sulfuric acid units in the United States employ vertical tube and vertical panel mist eliminators for stack gas mist control, 10 percent employ electrostatic precipitators, and 45 percent employ horizontal dual pad mist eliminators. Of the latter, not all employ the scrubbing action described in Section 6.2.1.3, not all operate with a pressure drop as high as 9 inches of H_2O, and not all are necessarily able to reduce emissions to 2.0 milligrams per cubic foot or less. It is known that at least 15 percent of the total sulfuric acid units in the United States employ horizontal dual pad mist eliminators which do meet these requirements. If the above percentages are accurate, they mean that about 5 percent of the sulfuric acid units in the United States do not have stack gas acid mist controls.

In 1971 about 70 non-metallurgical contact-process sulfuric acid plants were not covered by enforceable state regulations. Table 6.9 gives state regulations for acid mist emissions from existing plants as of July 1972 (24). Eighteen of the 41 states with sulfuric acid plants had enforceable regulations for existing plants. In addition, East Chicago, Indiana had a regulation of 0.5 lb mist/ton acid; and Wayne County, Michigan a regulation of 0.7 lb mist/ton acid. Eight states had a regulation of 0.15 lb mist/ton acid for new plants. All new plants must now meet the EPA new source performance standard of 0.15 lb mist/ton acid; states may adopt or enforce standards that are at least as stringent as the EPA standard.

TABLE 6.9

STATE REGULATIONS FOR ACID MIST EMISSIONS FROM EXISTING SULFURIC ACID PLANTS (24)

States	Lb H_2SO_4 Mist Per Ton of 100% H_2SO_4 Produced
Georgia, Illinois, Wyoming	0.15
New Hampshire	0.18
Alabama, Iowa, Kansas, Mississippi, Missouri, North Carolina, Ohio, Pennsylvania, South Carolina, Tennessee	0.5
Kentucky, Virginia	0.9
Minnesota	1.7
New Jersey	1.88

6.4 EMISSION GUIDELINE FOR EXISTING SULFURIC ACID PLANTS

Emission guidelines for existing sources must be based on applying the best available system of emission reduction, considering cost. For sulfuric acid plants, these guidelines apply to existing contact-process sulfuric acid and oleum facilities that burn elemental sulfur and chemically bound sulfur feedstocks such as alkylation acid, hydrogen sulfide, organic sulfides, mercaptans or acid sludge. These emission guidelines do not apply to acid plants used as SO_2 control systems, to chamber process plants, to acid concentrators, or to oleum storage and transfer facilities.

Based upon the rationale in Section 7 and the source test data in Section 6.3, the acid mist emission guideline for existing sulfuric acid plants that reflects the application of the best system of emission reduction considering cost is:

> No more than 0.25 g (measured as H_2SO_4) per Kg of acid (as 100 percent H_2SO_4) produced, or 0.5 lb per ton.

The reference method for determining acid mist emissions is EPA Method 8 of Appendix A to 40 CFR Part 60.

The emission guideline reflects the application of vertical panel or horizontal dual pad mist eliminators, as a minimum, to sulfur burning plants producing acid or low strength oleum. For plants burning bound sulfur feedstocks and/or producing strong oleum, the guideline reflects the application of vertical tube mist eliminators. However, there may be some bound sulfur feedstock or oleum plants capable of meeting the emission guideline with vertical panel or horizontal dual pad mist eliminators.

6.5 GOOD PRACTICES. (1)

The greater the acid mist loading to fiber mist eliminators, the greater the acid mist emissions from them to the atmosphere is likely to be. Hence to minimize acid mist emissions it is important to minimize acid mist formation in the acid production unit.

Good practices which minimize mist formation fall into three classes: those that apply to all units, those that apply to sulfur burning units only, and those that apply to units burning spent acid and other by-products. Good practices which apply to all units include those which minimize moisture to the converter, those which minimize acid spray to the converter, and those which minimize mist formation between the converter and the absorber.

To minimize moisture to the converter, make sure that:

1. The acid to the drying tower is at the proper strength. It should be between 93 and 99 percent H_2SO_4.
2. The acid to the drying tower is at the proper temperature. It should be below 120°F for a unit drying with 93 percent acid and below 170°F for a unit drying with 98 percent acid.
3. There is sufficient acid flow to the drying tower. A minimum acid flow is about 1.5 gallons per minute per ton of 100 percent H_2SO_4 produced.
4. The acid is properly distributed on the top of the packing in the drying tower.

5. The packing in the drying tower is clean.

6. If the blower is located after the drying tower, that atmospheric moisture is not drawn in the suction duct or connections of the blower.

To minimize acid spray to the converter which can cause moisture in the SO_3 gas leaving the converter make sure that:

1. Splashing is not occurring in the acid distribution system on the top of the drying tower.

2. Failure has not occurred in the drying tower entrainment separator.

3. Flooding has not occurred in the drying tower.

To minimize mist formation between the converter and the absorber, make sure that:

1. Cooling in the economizer is not too great, too fast, or localized.

2. Rainstorms or sudden changes in temperature and wind velocity have not caused duct cooling and subsequent mist formation. If atmospheric conditions appear to affect mist formation, duct shielding may be required.

3. If the unit is producing oleum, that leakage is not occurring in the SO_3 gas line bypassing the oleum tower.

The subsequent mixing of hot and cooled gas streams can generate mist.

Good practices which apply to sulfur burning units only include those which minimize nitrogen oxides in the burner, those which minimize steam or water leaks in the unit, and those which improve quality control of the sulfur.

To minimize nitrogen oxides, make sure that the sulfur burner temperature is below 2000°F. Very high burner temperature causes nitrogen to combine with oxygen and form nitrogen oxides.

The primary places where steam or water leaks can occur are in the sulfur line to the burner and in the process boilers and economizer.

To minimize acid mist formation stemming from the sulfur, it is important to have a suitable analytical quality control program. The two most important analyses to consider are hydrocarbon and moisture. Good sulfur filtering can sometimes help to reduce hydrocarbons, and proper storage and handling practices can help to reduce moisture.

Good practices which apply to units burning spent acid and other by-products include those which minimize mist carryover from the gas purification section and those which minimize nitrogen oxide formation.

To minimize mist carryover it is important that the dust and mist removal device in the gas purification section (usually an electrostatic precipitator) be operating efficiently.

To minimize nitrogen oxide formation, make sure that:

1. The burner temperature is below 2000°F.
2. Arcing is not occurring in the electrostatic precipitator which is in the gas purification section.

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7. ECONOMIC IMPACT

7.1 INTRODUCTION

This section develops the rationale for the selection of the emission guideline. The economic impact is analyzed for both captive and open market producers. The analysis is specific to the following industry categories: plants burning elemental sulfur and producing no oleum, plants burning bound sulfur feedstocks, and oleum producers burning any raw materials.

The emission guideline is a level not to exceed 0.5 lb of acid mist per ton of acid produced, when measured by EPA Method 8. This level will allow low-cost mist eliminators for the sulfur burning, H_2SO_4-producing plants. The remainder of the industry will be expected to install the more expensive vertical tube device.

Profits in general are currently high in the industry and will be sufficient to absorb any of the control costs for those plants needing retrofits wherever competitive forces may prevent price increases. The only adverse impact foreseen may occur for the sludge processing plants that sell much of their acid on the open market in competition with acid producers incurring lower production and control costs. Oleum producers, on the other hand, will be expected to pass on most of the costs.

7.2 INDUSTRY STRUCTURE

Over fifty percent of the sulfuric acid produced is consumed for phosphate fertilizers and ammonium sulfate fertilizers. Most of the acid produced for these uses is captive to the firms that manufacture fertilizers and is mainly derived from elemental sulfur.

The second largest use for sulfuric acid is alkylation in petroleum refining. Acid plants producing this acid use spent sludge acid from the refineries. These acid plants may either be captive or owned by chemical companies that specialize in processing such material. About eight percent of all sulfuric acid production is consumed by refineries.

The balance of sulfuric acid production and oleum is spread among many chemical manufacturing activities such as explosives, fibers (rayon, cellulose/acetate), pigments, batteries, aluminum sulfate, alcohols, phenol, and sulfonates. Acid produced for this segment of the industry is sold on the open market, hence the term merchant acid. Most oleum is sold as merchant acid for consumption in many of the above activities.

Pricing for sulfuric acid is sensitive to shipping volume and transportation costs. Concise information for a particular locale can only be obtained by contacting local suppliers or buyers. A wide range of prices exists in the industry, as demonstrated by the following information. Current quotes by the Chemical Marketing Reporter (Nov. 4, 1974) price acid at $43 to $50 per ton (at the acid plant). According to several contacts in the industry, these prices are what a customer pays for a small, one-time transaction. Contact with one large consumer (Gulf Coast) (1) and one large merchant acid seller (2), indicates prices ranging from $23 to $30 per ton delivered, for larger shipments. These lower prices represent long term contracts (consistent with large volume production) with escalation clauses protecting both acid producer and consumer against fluctuation in sulfur prices. Transportation is such an important factor that plants ideally located (with low transportation costs to the consumer) can favorably compete against lower cost producers that are remote.

Prices for oleum are difficult to establish. One seller (2) indicated that oleum carries a market premium over 100 percent acid on an equivalent weight basis (H_2SO_4 content). This premium or price spread increases with the percentage of SO_3. Contact with a buyer (1) revealed no existence of premiums. The conclusion from these contacts is that oleum and sulfuric acid are not always priced equally. Two factors that might reduce current premiums for oleum would be: more sulfuric acid producers converting to oleum production, or a decline in demand for oleum relative to acid. Air pollution control costs (specifically acid mist control costs), on the other hand, might be expected to prevent convergence of prices for oleum and sulfuric acid.

7.3 IMPACT ON MODEL PLANTS

The sulfuric acid industry consists of plants using different raw materials and selling sulfuric acid and various grades of oleum. Production costs will differ according to requirements for purification, feed stream drying, and pollution control. The cost structure of the industry is dependent upon many important production variables, notably: plant size, raw materials, plant design, and products.

Table 7.1 exhibits production costs for an elemental sulfur burning plant and a spent acid burning plant, both producing 1000 tons per day, 100 percent H_2SO_4. An acid price of $30 per ton delivered was arbitrarily set to represent a typical long-term contract. Freight costs were also arbitrarily set. According to one source (3), profits before taxes average about $2.40 per ton of acid for a utilization of 75 percent of capacity.

Pre-tax profits for the industry with the same utilization rate were estimated to vary from $1.00 per ton to $4.00 per ton, according to plant size. Table 7.1 shows significantly higher profits for

TABLE 7.1

PRODUCTION COSTS FOR EXISTING ACID PLANTS
(Built in period from 1968 to 1972)

	Elemental Sulfur	Spent Acid
Original Plant Capital ($1000)	3000	5400
Capacity, TPD	1000	1000
Production, TPY	328,000	328,000
Sales ($/T), Delivered	30	30
Sulfur Cost ($/T)	13.50	13.50(a)
Other Product Costs ($/T)(b)	3.52	7.72
Total Mfg. Costs ($/T)	17.02	21.22
Selling Expense, Administrative, Corporate Overhead ($/T)	2.50	2.50
Freight ($/T)	3.00(c)	2.00(d)
Operating Profit ($/T)	7.48	4.28
Income Taxes ($/T)	3.74	2.14
Profit After Taxes ($/T)	3.74	2.14

(a) Sulfur credit to refinery

(b) Includes air + water abatement costs to meet SIP's (SO_2 only) and water effluent guidelines, respectively. These costs are as follows:

> Elemental sulfur burning plant - air costs, $1.50 per ton; water costs, $0.50 per ton. Spent acid burning plants - air costs, $2.50 per ton; water costs, $1.00 per ton.

(c) Freight based on 150 miles via rail @ 2¢ per ton-mile one direction.

(d) Freight based on 100 miles round trip via rail @ 2¢ per-ton mile.

the case of the sulfur burning plant. This is expected due to the plant's large size (average plant size is 500 TPD). Also, rate of utilization of capacity is assumed to be 90 percent. In general, with high utilization today (at 90 percent) and high product demands, profits can be conservatively estimated to be approximately double the above estimate of $1.00-$4.00 per ton (3). The profit depicted for the spent acid plant ($2.14) is somewhat above the profit of the average-sized plant (500 TPD). However, a new sludge processing plant (for 1000 TPD production) would cost nearly $10 million in 1974, or $30 per annual ton capacity. The $2.14 profit thus amounts to a return on equity of approximately 7 percent. This is unattractive when compared with today's corporate borrowing cost of 10 percent. This is important to the refinery that may consider building its own captive sludge plant in lieu of paying the sludge processor for his controls. Environmental costs for abatement of SO_2 and for neutralization and settling of suspended solids for waste water discharges have been incorporated into the cost structures exhibited in Table 7.1. The costs for meeting SIP requirements on abatement of SO_2 are approximately $1.50 per ton of product for the elemental sulfur burning plant and $2.50 per ton for the sludge burning plant (4). However, the requirements for SO_2 abatement in SIP's are not the same in all states. Stage I water treatment guidelines costs (3) are $0.50 per ton and $1.00 per ton for the elemental sulfur and sludge burning plants respectively. Total environmental control costs before mist controls are thus approximately $2.00 per ton for the elemental sulfur plant and $3.50 for the sludge acid plant.

For a 1000 TPD elemental sulfur-burning acid plant, the least cost option of achieving the acid mist guideline will range from $0.04 to $0.11 per ton (interpolated from Table 6.2). For a spent acid-burning plant or a plant producing strong oleum operating at 1000 TPD acid, the cost of achieving the guideline would range from $0.34 to $0.65 per ton, the low end of the range representing "piggyback" installation and the high end representing "at grade" installation. These costs will be higher for the elemental sulfur-burning plant that may convert only a small portion of its acid to heavier grades of oleum. For such a plant producing 1000 TPD, the marginal cost to control acid mist per ton of oleum with a high efficiency vertical tube collector could be significantly more than $1.00 per ton. However, the average cost remains the same as for the acid sludge-burning plant and the full time oleum producer. The impact of this situation for the occasional oleum producer will be discussed in the next section.

7.4 RATIONALE FOR SELECTION OF GUIDELINES

Emission guidelines for existing sources must be based on applying the best available system of emission reduction considering costs. For sulfuric acid plants, the guideline applies to existing contact-process sulfuric acid and oleum facilities that burn elemental sulfur and chemically bound sulfur feedstocks such as alkylation acid, hydrogen sulfide, organic sulfides, mercaptans, or acid sludge. Practicable retrofits for controlling acid mist emissions from these plants include vertical tube, vertical panel and horizontal dual pad mist eliminators. The emission guideline does not apply to metallurgical acid plants, to chamber process plants, to acid concentrators, or to oleum storage and transfer facilities.

Based upon equipment capabilities, existing State standards, emission test data, and best demonstrated control technology for new plants (the EPA acid mist standard of performance for new sulfuric acid plants), four alternative control levels could be proposed as candidates for the emission guideline. Table 7.2 lists these levels and the corresponding control equipment required.

TABLE 7.2

ALTERNATIVE ACID MIST CONTROL LEVELS AND CORRESPONDING CONTROL EQUIPMENT

	Required Control Equipment	
Candidate Control Level (lb mist/ton 100% H_2SO_4)	Oleum Plants and Bound Sulfur Feedstock Acid Plants	Sulfur Burning Acid Plants
2.0	Vertical panel and horizontal dual pad	Vertical panel and horizontal dual pad
0.5	Vertical tube (commonly)	Vertical panel and horizontal dual pad
0.3	Vertical tube	Vertical tube
0.15	Vertical tube	Vertical tube

The 2.0 pound control level is based upon the capabilities of the vertical panel and horizontal dual pad mist eliminators applied to oleum plants and bound sulfur feedstock acid plants, and the fact that not one of the 18 state standards for existing plants is higher than this level (see Table 6.9, Section 6.3.4).

The 0.5 pound control level is based upon the capabilities of the vertical panel and horizontal dual pad mist eliminators applied to sulfur burning acid plants, and the fact that 14 of the 18 states with standards for existing plants have standards at or below this level. For oleum plants and for bound sulfur feedstock acid plants, the vertical tube mist eliminator is usually required to achieve the 0.5 pound control level.

The 0.3 lb/ton level is based on the test data in Tables 6.5, 6.6, and 6.7. Most of those data are well below 0.3 lb/ton, and only two individual runs exceeded 0.3 lbs/ton. Assuming the two high runs are valid, when averaged with other runs as is done for a performance test, the plant would be in compliance with a 0.3 lb/ton standard. This level of control would require vertical tube mist eliminators on most sulfuric acid plants.

The 0.15 pound control level is based upon best demonstrated control technology for new plants as specified in the EPA standard of performance for new plants. This standard is based on source tests at plants producing oleum as well as acid, and burning elemental sulfur and other feedstocks. Of the types of devices considered, the vertical tube mist eliminator is the only one that will allow any type of sulfuric acid plant to achieve the 0.15 pound control level.

The following discussion deals with the economic impact and other issues associated with each of the candidate levels.

2.0 lb/ton

The 2.0 lb. level of control corresponds to control which would be achieved by application of the vertical panel or horizontal dual pad across the board. All states with regulations for acid mist had levels lower than the 2.0 lb guideline, and thus, this candidate level was dismissed since it does not represent application of best control technology, considering cost.

0.5 lb/ton

The 0.5 lb. level of control can be achieved on sulfur burning acid plants with vertical panel and horizontal pad mist eliminators. For the plants considered in Table 6.2, the least cost option of control will range from $0.03 to $0.42 per ton of acid, over the 50 TPD to 1500 TPD plant sizes, with lower costs favoring the larger plants. This level of control will generally require the use of the more expensive vertical tube mist eliminator on oleum plants producing the higher grades of oleum, and on bound sulfur feedstock acid plants. The tube mist eliminator will cost from $0.49 to $1.69 per ton for the 50 TPD to 1500 TPD plant for the at-grade retrofit (see Table 6.2).

It should be noted that industry feels that the pad type mist eliminators will meet acid mist standards of 0.5 lb/ton in plants burning bound sulfur feedstocks and making strong oleum. Data for plants A, H and I in Table 6.7 indicate this may be true in many cases; however, EPA doubts that it is universally true because vendors of the two kinds of pad mist eliminators will not guarantee their products for the 0.5 lb/ton level for oleum plants.

In addition, a comparison of superficial gas velocities through the pad and the tubular mist eliminators shows 400-600 ft/min for the pads and only 20-40 ft/min for the tubular. Thus, the pad removes mist particles by the single mechanism of inertial impaction; the tubular mist eliminator removes mist by the three mechanisms of inertial impaction for large particles, direct interception for smaller particles, and Brownian movement for sub-micron particles.

As indicated in Table 4.2, oleum production results in a finer particle size distribution than acid production and the mist becomes finer with increasing oleum strength. Consequently, oleum mist is best removed by the tubular mist eliminator because its performance is not much affected by changes in plant production rate and has a good turndown ratio.

In this case where the guideline will likely require different control equipment for oleum plants, EPA feels that the guideline is justified because: (1) oleum is a different product from acid; (2) oleum production is a different process from acid production and requires more complex plants, and (3) oleum has different markets and end uses than acid. Thus, oleum plants may be considered a subcategory of acid production units requiring different controls than acid plants do and it is economically reasonable for oleum plants to spend more for controls.

A State standard of 0.5 lb per ton would be expected to create no adverse impact for sulfur burning acid plants and minimal adverse impact for the oleum producers and spent acid processors. Control costs could be passed on or readily absorbed at the present high profitability in the industry. Only the sludge plant that operates extensively in open markets may find difficulty in absorbing the control costs or passing them on to its merchant acid customers. In comparison with sulfur burning acid producers, this sludge processor will have relatively higher control costs and lower profit margins before implementation of mist controls. The only outlet for sharing the cost burden of the sludge processor is the source of the sludge--the refinery. The refiner will either have to build his own acid plant or assist in paying for the portion of the control costs that cannot be transferred to the merchant acid market or absorbed by the sludge processor. In the short run, the refiner will be expected to prefer paying the mist control costs because, as stated in section 7.3, he would find that the alternative of building an acid plant would be an unattractive proposition.

The producers of oleum would handle their control costs in much the same way as would the sludge processing acid plant engaged in significant merchant acid sales. The costs for the control device can be partially passed on to the oleum consumer to the extent allowed by the price elasticity of demand on the part of oleum consumers. Whenever the consumer needs the SO_3 content of oleum as a carrier for reactions, drying, etc., he will be willing to pay a little more than the current sulfuric acid price. By contrast, the consumer buying oleum strictly for the freight savings will not be willing to pay additional control costs.

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The occasional oleum producer would probably be forced to absorb more of his control costs than his competitors who sell sulfuric acid or oleum as their only product. Since the size and total investment of a mist eliminator are based upon the entire plant's oleum and acid production, the incremental costs for the tube over the panel or pad are too large to be borne by the oleum consumers alone. Attempts to pass costs on to the acid consumers will be limited by competition from acid producers incurring both lower production and control costs. As a result, the occasional oleum producer will have to absorb those costs that cannot be passed on to his consumers. Since most oleum producers generally sell both acid and oleum, there doesn't appear to be any individual producers in an unfavorable trade position who would suffer an adverse impact from the recommended emission limitation. Vendors refuse to guarantee the performance of panels and pads on oleum plants, and most State standards are 0.5 lb/ton or lower. For these reasons, occasional oleum producers would have installed vertical tubes and/or adjusted their market position.

0.15 lb/ton

The 0.15 lb level of control can be achieved only by installation of the vertical tube mist eliminator on all acid plants. Such a level would create adverse economic impact for smaller, older plants that are faced with both acid mist and SO_2 abatement. On the other hand, high costs of achieving the 0.15 lb. limitation can be more easily absorbed by plants that do not require a strict level of SO_2 abatement (such as that associated with dual absorption or tail gas scrubbing). With the uncertainty in establishing SO_2 controls, the problem of quantifying the impact is difficult.

An important element that would contribute to the adverse economic impact on the industry is the resultant double retrofitting of controls that would be required by the 0.15 level. It is estimated that 40 percent of all sulfuric acid units in the United States have vertical tube or vertical panel mist eliminators and 15 percent have horizontal dual pad mist eliminators capable of meeting the 0.5 pound control level. If one-half of the vertical mist eliminators are panels, then it follows that 35 percent of all sulfuric acid units (20 percent, vertical panels; 15 percent, pads) are exceeding the 0.15 pound level, but meeting the 0.5 pound level. If the above acid unit percentages are comparable on an acid plant basis, and if all the vertical panel and horizontal dual pad mist eliminators are installed on the 45 percent of the U.S. plants that burn sulfur and do not produce oleum, then 78 percent (35 of 45) of these would be forced to retrofit. If only 10 percent of all acid plants can be assumed to have vertical panels, then 56 percent (25 of 45) of the sulfur burning, H_2SO_4-producing plants would still be forced to double retrofit.

To undergo double retrofit expenditures at a time when fertilizer production capacity is tightly constrained (over fifty percent of the sulfuric acid produced goes into fertilizers) would further aggravate contemporary world food shortage problems. In addition, many of the fertilizer industry's sulfuric acid plants have been compelled to undergo major expenditures to limit SO_2 emissions to a level equivalent with performance of dual absorption acid plants.

0.3 lb/ton

Since for most acid plants 0.3 lb/ton can be achieved only with a vertical tube mist eliminator, the problems of double retrofitting discussed for the 0.15 lb/ton level also apply. While the data in Tables 6.5, 6.6, and 6.7 are almost all below 0.3 lb/ton, the data base is limited, since two of the plants in Table 6.5 operated substantially below capacity, plants in Table 6.6 produced no oleum, and the data in Table 6.7 are from sources other than EPA tests.

Another consideration is the vendor guarantees of 2.0 mg/scf for a vertical panel or horizontal dual pad mist eliminator. Plant E (Table 6.6) has a converter inlet concentration of seven percent SO_2. From Figure 4.1, 2.0 mg/scf is equivalent to 0.45 lb/ton of acid mist. Thus, the vendor guarantee might prohibit installation of a vertical panel or horizontal pad mist eliminator to comply with a 0.3 lb/ton emission standard.

Finally, the emission guideline requires more than control of particulate acid mist; it also requires control of H_2SO_4 vapor and

SO_3 through proper absorber operation and design. Even in properly operated plants the theoretical amount of H_2SO_4 and SO_3 vapor, measured as H_2SO_4, can amount to over 1 lb/ton acid produced. To further reduce the vapor emissions would require increased absorber height and power costs. Since EPA Method 8 measures a small fraction of the vapor emissions, the mist eliminator, which controls only the particulate acid mist, must be capable of reducing mist emissions to a level of the EPA guideline minus the fraction of H_2SO_4 and SO_3 vapors measured by Method 8. Thus because of the uncertainty of the amount of vapor measured, a plant owner might be compelled to install a vertical tube mist eliminator to insure compliance with a standard of 0.3 lb/ton.

Because Reference Method 8 does measure an unknown fraction of the SO_3 and H_2SO_4 vapor, there has been some question regarding the precision and accuracy of the method. Results of a collaborative test performed in 1974 showed poor precision for the method (5). Recent review of this study indicates that the problem may be due to the collaborative test procedure and not due to Method 8. Specifically, because the high values of acid mist collected on any run were accompanied by comparatively low results for SO_2, it is likely that contamination of the isopropanol solution occurred prior to the test, either through poor preparation or by back flushing hydrogen peroxide solution during the leak check. This contamination would cause some of the SO_2 to be counted as acid mist. As a result of the apparent problems with this study, EPA is commencing a study to further investigate the isopropanol contamination problem and to establish the precision of the method. If these studies indicate a problem, EPA will make appropriate revisions to Reference Method 8 and the emission guideline. As pointed out in section 6.3.2, for sulfur burning acid plants the EPA and Monsanto methods have shown a good correlation, and thus major problems with the method are not expected.

EPA's position regarding the accuracy of the method is that as long as the compliance test method is consistent with the method used to develop the emission guideline (Method 8), it is not necessary to know the absolute concentration of acid mist in the stack. Thus in compliance testing, the repeatability (precision) is more critical than the accuracy.

Dual Guideline

During the course of the development of the guideline some consideration was given to setting a 0.15 lb guideline for plants producing oleum and/or burning bound sulfur feedstocks, and a 0.50 lb. guideline for sulfur burning, H_2SO_4-producing plants. The approach was rejected due to a lack of supportive emission data over a wide enough range of operating conditions for plants producing oleum and/or burning bound sulfur feedstocks. Furthermore, many plants make oleum on a part-time basis, based on market demand. Thus, these plants could be required to install the most expensive control for a few runs per year if EPA promulgated a dual guideline (relief under §60.24(f) could possibly mitigate this problem).

Summary

In summary, industry-wide adverse impacts are not expected for the recommended emissions guideline of 0.5 lb/ton. However, there may be a few isolated cases where a sludge processing plant may have difficulty if the plant is not captive to a petroleum refinery. Depending on their product mix or sulfuric acid and oleum, oleum producers will pass on to a greater or lesser extent their control costs. No problems are foreseen for any individual oleum producer that may sell oleum only in small quantity.

The cost analysis which resulted in a guideline of 0.5 lb/ton was influenced by the double retrofitting involved with a guideline less than 0.5 lb/ton. However, where double retrofitting is not a problem (i.e., in States with plants in compliance with existing standards more stringent than the guideline, or for presently uncontrolled plants), State standards as low as the standard of performance for new sources (0.15 lb/ton) may be justified.

7.5 REFERENCES FOR SECTION 7.

1. Personal communication from R. C. Lamos, Dow Badische Co., Williamsburg, Virginia, to F. L. Bunyard, Strategies and Air Standards Division, OAQPS. Environmental Protection Agency, Research Triangle Park, N.C. November 19, 1974.

2. Personal communication from F. Koontz, Cities Service Co., Industrial Chemicals Division, Atlanta, Georgia, to F. L. Bunyard, Strategies and Air Standards Division, OAQPS, Environmental Protection Agency, Research Triangle Park, N.C. November 18, 1974.

3. Study of the Economic Impact of the Cost of Alternative Federal Water Quality Standards on Ten Inorganic Chemicals. Booz-Allen & Hamilton. Washington, D.C. Prepared for Environmental Protection Agency. December 4, 1972.

4. LeSourd, D.A. and F.L. Bunyard. Comprehensive Study of Specified Air Pollution Sources to Assess the Economic Impact of Air Quality Standards. Research Triangle Institute. Research Triangle Park, N.C. Prepared for Environmental Protection Agency under Contract No. 68-02-0088. Report No. FR-41U-649. August 1972.

5. Hamil, H. F., D. E. Camann, R. E. Thomas. Collaborative Study of Method for the Determination of Sulfuric Acid Mist and Sulfur Dioxide Emissions from Stationary Sources. Southwest

Research Institute. San Antonio, Texas. Prepared for Environmental Protection Agency under Contract No. 68-02-0626, EPA 650/4-75-003. November 1974.

8. ENVIRONMENTAL IMPACT

8.1 ENVIRONMENTAL IMPACT OF THE EMISSION GUIDELINE

The assessment of the environmental impact of the emission guideline is based on the incremental impact above that normally imposed on the environment by the affected sources or process controlled to meet other pollution regulations such as State Implementation Plans (SIP) or local regulations. The environmental impact is therefore a function of incremental effects, or a comparison of two degrees of control, and is not the total effect of the pollution control itself.

8.1.1 Air Impacts

8.1.1.1 Changes in mass emission rates

In Section 6.3.4, it was estimated that 95 percent of the sulfuric acid units in the United States have acid mist controls. Stack gas control equipment capable of meeting the emission guideline of 0.5 lb acid mist/ton H_2SO_4 produced (lb/ton) includes vertical tube, vertical panel and horizontal dual pad fiber mist eliminators; and electrostatic precipitators. According to Section 6.3.4, at least 65 percent (40-tube and panel; 15-dual pad; 10-ESP) of all acid units have such controls. The most common State acid mist regulation is 0.5 lb/ton, a level adopted by 10 of the 18 states with enforceable regulations, listed in Table 6.9. Four states have higher standards; four have lower ones. Hence, the greatest impact will be around the 35 percent of acid plants which presently do not have adequate mist eliminators. In addition, State standards will require those plants which have mist eliminators to maintain and operate the control systems properly, which will yield a beneficial, but unquantifiable air impact.

An average-sized sulfuric acid plant has a capacity of about 500 TPD. For a 500 TPD acid (vs. oleum) plant operating 350 days per year, an uncontrolled emission rate of 4.0 lb/ton (see Section 4.3) is equivalent to an emission of 350 tons/year. For a 500 TPD oleum plant, an uncontrolled emission rate of 10.0 lb/ton is equivalent to an emission of 875 tons/year. If either the acid or the oleum plant is controlled to the level of the emission guideline and most State regulations (0.5 lb/ton), the emission for the plant is reduced to 44 tons/yr. For a 500 TPD plant, each emission increment of 0.1 lb/ton is equivalent to a difference in emission of 8.75 tons/yr.

About one third of the U.S. sulfuric acid plants produce oleum while two-thirds do not (see Table 2.3). Hence, on a national basis, an average uncontrolled emission rate is about 6.0 lb/ton--[2 (4) + 1

(10)] / 3. This rate is equivalent to an emission of 95,000 tons/year at the 1973 sulfuric acid production level of 31.7 million tons per year. Control at the 0.5 lb/ton level reduces this emission to 7925 tons/year. Each emission increment of 0.1 lb/ton is equivalent to a difference of 1585 ton/year.

8.1.1.2 Atmospheric dispersion

A dispersion analysis was made for several plant sizes, types, and averaging times. Ground level concentrations were calculated for both controlled and uncontrolled plants. The methodology and assumptions used are summarized in Appendix A. Results of this analysis are presented in Table 8.1. As can be seen from the results, controlling plants to a level of 0.5 lbs per ton of acid has a tremendous impact on ground-level concentrations compared to the uncontrolled plants.

Estimates presented in Section 6.3.4 indicate that 5 percent of the sulfuric acid plants in the U.S. do not have acid mist control systems. Since 27 states either have no regulations or regulations less stringent than the emission guideline, it may be assumed that the ground-level concentrations in Table 8.1 from the uncontrolled plants are an upper bound to the concentrations actually observed in those states. Application of state standards at least as stringent as the emission guideline will result in significant reductions in ground-level concentrations.

TABLE 8.1 DISPERSION ANALYSIS RESULTS

Plant Size (tons per day)	Averaging Time	CONCENTRATION ($\mu g/m^3$)						Distance From Source (km)
		Controlled to (lb mist/ton acid)				Uncontrolled Acid Plant	Uncontrolled Oleum Plant	
		0.15	0.3	0.5	2.0			
50	10 sec.	24	48	80	320	640	1600	0.3
	1 hr.	1.5	3	5	20	40	100	0.3
	24 hr.	0.2	0.4	1	1.5	3	16	0.6
	Annual Avg.	0.04	0.08	0.2	0.3	0.6	3	0.6
250	10 sec.	56	112	185	740	1480	3700	0.6
	1 hr.	4	8	12	48	96	240	0.6
	24 hr.	0.7	1.4	2	10	19	47	1.4
	Annual Avg.	0.1	0.2	0.4	2	4	9	1.4
750	10 sec.	66	132	220	880	1760	4400	0.9
	1 hr.	4	8	14	56	112	280	0.9
	24 hr.	1	2	3	12	24	60	2.1
	Annual Avg.	0.2	0.4	0.6	2.5	5	12	2.1
1500	10 sec.	66	132	220	880	1760	4700	1.3
	1 hr.	4	8	14	56	112	300	1.3
	24 hr.	1	2	3	12	24	60	2.7
	Annual Avg.	0.2	0.4	0.6	2.5	5	12	2.7

8.1.1.3 Effects on other air pollutants

Sulfur dioxide (SO_2) is the air pollutant emitted in greatest quantity from sulfuric acid plants. Like acid mist, its principal emission point is the stack gas from the final absorber. Installation of stack gas acid mist control devices will not change the quantity of SO_2 emitted. Furthermore, their installation will not generate any additional secondary air pollutants.

Nitrogen oxides may be present in the converter exit gas stream, especially in spent acid plants. As discussed in Section 4.2.3, they react with SO_2 and sulfur trioxide (SO_3) to form very fine mists. These mists will pass through the final absorber and through impaction mist control devices like vertical panel and horizontal dual pad mist eliminators. High efficiency vertical tube mist eliminators will remove most of this mist from the stack gas.

8.1.2 Water Pollution Impact

The sulfuric acid collected by acid mist controls is returned to the process. Hence there is no effluent discharge at any acid mist air pollution control level. However, some of the acid mist discharged from the stack will fall out in the vicinity of the plant and may be washed out by rainfall. Ground runoff can cause some of this acid fallout to eventually reach local watercourses; however, it is more likely to react with the calcium carbonate or other acid-consuming constituents of the soil and so lose its acid character.

8.1.3 Solid Waste Disposal Impact

Because acid mist controls do not generate or recover solid waste there is no solid waste disposal impact.

8.1.4 Energy Impact

The guideline has little energy impact because the electrical energy requirements associated with fiber mist eliminators are small and most plants already have some type of fiber mist eliminator. For example, an energy penalty of 3.6 kilowatt-hours (KWH) per ton of acid produced can be calculated based upon a fiber mist eliminator pressure drop of 10 inches of H_2O, a fan efficiency of 55 percent and an acid plant process air requirement of 71 acfm per ton of acid produced.

The reduction in emissions from installation of fiber mist eliminators far outweighs the additional pollution emitted by a power plant in generating the mist eliminator's attendant electrical requirement. For example, such an installation will reduce the acid mist emission rate from a typical acid (vs. oleum) plant from 4.0 to 0.5 lb/ton, a reduction of 3.5 lb/ton. From the preceding paragraph, a typical attendant energy penalty is 3.6 KWH/ton. This is equivalent to 37,800 BTU heat input per ton of acid produced, assuming a power plant heat input requirement of 10,500 BTU/KWH. If the electricity is generated in a coal-fired plant complying with the EPA standards of performance for new stationary sources, then particulate, SO_2, and nitrogen oxide (NO_x) emissions are restricted to 0.2, 1.2 and 0.7 lb per million BTU heat input, respectively. For a heat input of 37,800 BTU, corresponding emissions of particulate, SO_2 and NO_x are 0.008, 0.045 and 0.027 lb per ton of acid, respectively, or a total of 0.08 lb/ton. Thus in this example, the electrical energy associated with one pound of air pollution at the power plant will help eliminate 44 pounds (3.5/0.08) of air pollution when delivered to a fan supplying an acid plant mist eliminator pressure drop requirement of 10 inches of H_2O.

8.1.5 Noise Effects

The emission guideline has no noise impact because fiber mist eliminators and final absorbers operate with no detectable noise. When retrofitting fiber mist eliminators, an additional fan may be needed to handle the increased pressure drop (See Section 6.2.2.1). This fan may slightly increase the plant's noise level.

8.1.6 Other Environmental Concerns

There are no other environmental concerns - such as an increase in radiative heat or in dissipated static electrical energy - related to the level of the emission guideline.

8.2 ENVIRONMENTAL IMPACT UNDER ALTERNATIVE EMISSION CONTROL SYSTEMS

The emission guideline is based upon the capabilities of fiber mist eliminators. No alternative emission control system meets the requirements of best demonstrated control technology considering cost. Although mild steel electrostatic precipitators effectively control acid mist, their large size makes retrofit installation costs high, and they are expensive to maintain in a corrosive acid environment.

8.3 SOCIO-ECONOMIC IMPACTS

Minimal adverse socio-economic impact should result from the emission guideline. The only adverse economic impact foreseen may occur for the sludge processing plants competing on the open market (See Section 7). In 1967, the sulfuric acid industry employed 4,500 persons.[1] Hence closure of an average-sized plant would mean employment loss for about 20 people. However, no plant closures or loss of employment are anticipated.

8.4 OTHER CONCERNS OF THE EMISSION GUIDELINE

The emission guideline should not have any other adverse or beneficial environmental effects. It will not create short-term environmental gains at the expense of long-term environmental losses or vice versa, and will not result in irreversible and irretrievable commitment of resources. It will not foreclose future control options or curtail the diversity and range of beneficial uses of the environment.

8.5 REFERENCE FOR SECTION 8

1. 1967 Census of Manufacturers. Bureau of the Census, U. S. Dept. of Commerce, Washington, D. C. Vol, II, Industry Statistics, Part 2. January 1971. p. M28A-43.

APPENDIX A - DISPERSION ANALYSIS METHODOLOGY AND ASSUMPTIONS

The diffusion analysis results of Table 8.1 were generated by the Source Receptor Analysis Branch, EPA using the Single Source Model developed by the Meteorology Laboratory, EPA. The model is designed to estimate concentrations due to sources at a single location for averaging times from one hour to one year.

This model is a Gaussian plume model using diffusion coefficients suggested by Turner (1970).[1] Concentrations are calculated for each hour of the year, from observations of wind direction (in increments of 10 degrees), wind speed, mixing height, and atmospheric stability. The atmospheric stability is derived by the Pasquill classification method as described by Turner (1970). In the application of this model, all pollutants are considered to display the dispersion behavior of non-reactive gases.

The 10-second concentrations in Table 8.1 were calculated manually from the one-hour concentrations, using Eq 5.12 (p. 38) of Turner's "Workbook of Atmospheric Dispersions Estimates." Based on the advice of Mr. Turner, a strong dependence on stability class was incorporated into the equation. Specifically, the exponent "p" varies from about 0.67 to about 0.17 as stability class varies from A to F. The plants in this study exert their greatest impact under very unstabled ("A") conditions, and therefore an exponent of 0.67 was used.

Meteorological data for 1964 are used as input to the model. The reasons for this choice are: (1) data from earlier years did not have sufficient resolution in the wind direction; and (2) data from subsequent years are readily available on magnetic tape only for every third hour.

Mixing height data are obtained from the twice-a-day upper air observations made at the most representative upper air station. Hourly mixing heights are estimated by the model using an objective interpolation scheme.

A feature of this model is the modification of plume behavior to account for aerodynamic effects for plants in which the design is not optimal. These effects result from the interaction of the wind with the physical structure of the plant. The extreme case is commonly referred to as "downwash." With downwash, the effluent is brought downward into the wake of the plant, from which point it diffuses as though emitted very close to the ground. In the retardation case, some of the dispersive benefits of plume rise are lost; while in the downwash case, all of the benefits of plume rise are lost, along with most of the benefits of stack elevation. Both phenomena - but especially downwash - can seriously increase the resulting ambient air impact.

The aerodynamic-effects modification then, is an attempt to include these effects in a predictive model. It was developed within EPA, and while not yet validated, is the best known operational approach. Basically, it enables the model to make an hour-by-hour, stack-by-stack assessment of the extent (if any) of aerodynamic complications. The parameters used in making the assessment are wind speed, stack-gas exit velocity, stack height, stack diameter, and building height. If a particular assessment indicates no aerodynamic effect, then for that stack (for that hour) the model behaves just as the unmodified version. If there are aerodynamic effects, the modified version contains equations by which the impact of these effects on ground-level concentrations is estimated. Aerodynamic effects were not a factor in this study due to favorable stack heights assumed.

Calculations are made for 180 receptors (at 36 azimuths and five selectable distances from the source). The model used can consider both diurnal and seasonal variations in the source. Separate variation factors can be applied on a monthly basis to account for seasonal fluctuations and on an hourly basis to account for diurnal variations. Another feature of the model is the ability to compute frequency distributions for concentrations of any averaging period over the course of a year. Percentages of various ranges in pollutant concentrations are calculated.

The following assumptions were applied in the analytic approach:

1. Mist was considered to behave as a non-reactive gas.
2. The plant is located in flat or gently rolling terrain with a meteoroligical regime which is unfavorable to the dispersion of pollutants. The effect of the latter is to introduce an element of conservatism into the analysis. In a restrictive terrain, the dispersion of pollutants could be even more impaired resulting in higher ambient concentration levels.
3. There are no significant seasonal or hourly variations in emission rates for this plant.
4. Source characteristics assumed are in Table A-1.

Table A-1

Plant size (TPD)	50	250	750	1500
Stack ht (m)	46 (150 ft)	46 (150 ft)	61 (200 ft)	76 (250 ft)
Stack diam. (m)	0.6 (2 ft)	0.9 (3 ft)	1.5 (5 ft)	2.1 (7 ft)
Stack Temp. (K)	344	344	344	344
Exhaust gas volume m^3/sec	1.64	8.2	25.1	50.6
Exhaust gas velocity (m/sec)	5.8	12.9	14.2	14.6
Emission rate (g/sec)				
Controlled to 0.5 lb/ton	0.13	0.66	1.97	3.94
Uncontrolled	1.0 acid 2.6 oleum	5.3 acid 13.2 oleum	15.8 acid 39.4 oleum	31.5 acid 78.3 oleum

Reference

1. Turner, D. B., "Workbook of Atmospheric Dispersion Estimates," U. S. Department of H.E.W., PHS Publication No. 999-AP-24 (Revised 1970).